(54) Title: BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMS

(57) Abstract

Improved biocidal composition and method for controlling biofouling and microorganism population levels in recirculating water systems such as cooling towers, swimming pools or spas is disclosed and claimed. The composition comprises a hypochlorite donor and a bromide ion donor in proportions selected to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20. The method comprises introducing into the recirculating water a mixture or combination of a hypochlorite donor and a bromide ion donor in an amount sufficient to maintain a ratio of the sum of all bromine containing species to the sum of all species in the recirculating water in the range of about 0.2 to about 20. In addition, a bromine volatilization suppressant may be introduced into the recirculating water to inhibit loss of bromide ion through volatilization of bromine containing species formed by reaction of the hypochlorite donor and the bromide ion donor. One or more scale inhibitors and compacting aids may also be added.

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BIOCIDAL METHODS AND COMPOSITIONS FOR RECIRCULATING WATER SYSTEMS

BACKGROUND OF THE INVENTION

1.   Field of the Invention

5   This invention relates to the disinfection of water
and to the control of biofouling in recirculating water
systems such as cooling towers, evaporative condensers,
air washers, swimming pools, hot tubs, and spas.

10   The invention more especially concerns methods and
compositions for controlling biofouling and microorganism
population levels in such systems wherein water soluble
hypochlorite donors and bromide ion donors are added to
the systems so as to improve biocidal effectiveness with
15 reduced costs.

         As used herein, the term "hypochlorite donor" means
any compound that will generate hypochlorite species when
dissolved in water.
20

         The term "bromide ion donor" means any compound that
will generate bromide ions when dissolved in water.

         The term "available halogen" means the standard form
25 for expressing the strengths or capacities of halogenating
chemicals as well as for the doses in which they are
applied and for the hypohalite species ($HOCl$, OCl^-, $HOBr$,
OBr^-) which remain in the water.

30   The term "available chlorine" means the same as
"available halogen", but refers specifically to chlorine
compounds.

         The term "available bromine" means the same as
35 "available halogen", but refers specifically to bromine
compounds.

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The term "hypohalite species" means hypochlorous acid, hypochlorite ion, hypobromous acid and hypobromite ion.

5   The term "hypochlorite species" means hypochlorous acid and hypochlorite ion.

The term "hypobromite species" means hypobromous acid and hypobromite ion.

10

The term "bromine species" means hypobromous acid, hypobromite ion, and bromide ion.

The terms "free halogen" and "free available halogen"
15 are used interchangeably and are defined as the concentration of halogen existing in the water as hypohalous acid, HOX, and hypohalite ion, OX⁻, where X is Cl or Br.

20   The terms "free chlorine" and "free available chlorine" are used interchangeably and are defined as the concentration of chlorine existing in the water as hypochlorous acid, HOCl, and hypochlorite ion, OCl⁻.

25   The terms "free bromine" and "free available bromine" are used interchangeably and are defined as the concentration of bromine existing in the water as hypobromous acid, HOBr, and hypobromite ion, OBr⁻.

30   The terms "combined halogen" and "combined available halogen" are used interchangeably and are defined as the concentration of halogen existing in the water in chemical combination with ammonia or organic nitrogen compounds.

35   The terms "combined chlorine" and "combined available chlorine" are used interchangeably and are defined as the

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concentration of chlorine existing in the water in
chemical combination with ammonia or organic nitrogen
compounds.

5   The terms "combined bromine" and "combined available
bromine" are used interchangeably and are defined as the
concentration of bromine existing in the water in chemical
combination with ammonia or organic nitrogen compounds.

10   The terms "total halogen" and "total available
halogen" are used interchangeably and are defined as the
sum of "free halogen" (or "free available halogen") and
"combined halogen" (or "combined available halogen").

15   The terms "total chlorine" and "total available
chlorine" are used interchangeably and mean the same as
"total halogen" and "total available halogen" but
specifically refer to chlorine.

20   The terms "total bromine or "total available bromine"
are used interchangeably and mean the same as "total
halogen" and "total available halogen" but specifically
refer to bromine.

25   The symbol "FAvC" represents "free chlorine" and
"free available chlorine" concentrations in the water.

         The symbol "AvC" represents the available chlorine
content of the hypochlorite donor.

30
         The term "halogen demand" is defined as the amount of
halogen which must be added to the water over a specific
period of time to maintain the "free halogen" and/or "free
available halogen" at a specific concentration in the

35 water.

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The term "chlorine demand" means the same as the "halogen demand" but specifically refers to "free chlorine" and/or "free available chlorine" concentrations.

5   The term "chlorinated isocyanuric acid derivative" means chlorinated isocyanuric acid including dichlorinated and trichlorinated isocyanuric acid, alkali metal and alkaline earth metal salts of chlorinated isocyanuric acid, and hydrates, complexes and mixtures thereof.
10

The term "hydantoin derivative" means an unsubstituted, halogenated (i.e. chlorinated or brominated), or alkylated hydantoin.

15   The term "sulfamic acid derivative" means unsubstituted, halogenated, or alkylated sulfamic acid.

The term "sulfonamide derivative" means halogenated, alkylated, or arylated sulfonamide.
20

The term "glycoluril derivative" means unsubstituted, halogenated, or alkylated glycoluril.

The term "succinimide derivative" means
25 unsubstituted, halogenated, or alkylated succinimide.

The term "oxazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated oxazolidinone.
30

The term "imidazolidinone derivative" means an unsubstituted, halogenated, alkylated, or arylated imidazolidinone.

35   The term "halogen concentration (free chlorine basis or free available chlorine basis)" means the halogen

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concentration in terms of free available chlorine,
regardless of whether the halogen species are
hypochlorite, hypobromite or mixtures thereof.

5   2.   Related Art

Cooling towers are used to provide cooling for the
air conditioning systems of office buildings, hotels and
hospitals and to provide cooling for industrial processes.
10   The water in these towers is subject to contamination from
the air blown through the tower and from the fresh water
used to compensate for evaporative losses and blowdown.
The contamination consists of both inorganic and organic
debris as well as live microorganisms capable of growing
15   and multiplying if suitable conditions are provided.
Formation of microbial deposits, known as biofouling, can
occur on almost any surface exposed to an aqueous
environment, causing substantial energy losses due to
increased heat transfer resistance. For this and other
20   reasons, cooling towers are adversely affected by
microorganisms, e.g. bacteria, fungi, molds, and algae, by
either sheer numbers of organisms, metabolic waste
products generated, health hazards presented, or deposits
created. Unfortunately, cooling towers provide many of
25   the conditions ideal for microbial growth, namely
favorable temperatures and moisture levels, and favorable
concentrations of air and nutrients.

Air washers are used to cool, cleanse, and humidify
30   the air in office buildings, factories, shopping malls,
and the like. Due to the large amount of air drawn
through the water, the growth of microorganisms is again a
problem. Since the air is used directly for inhabited
areas, the toxicity and odor of any compounds used for
35   treatment of the water in the air washers must be
extremely low.

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Similarly, water in swimming pools, hot tubs and spas must be sanitized in order to control disease spreading microorganisms. As with air washers, the toxicity and odor of compounds used to treat the water must be
5   extremely low.

It is customary to treat biologically contaminated water with one or more biocides to control the population of microorganisms in the water, to prevent fouling of heat
10   exchanger surfaces, and to prevent the spread of disease. The biocides most commonly used to disinfect and sanitize water in recirculating water systems are chemicals that generate hypochlorite species when dissolved in water. There are many hypochlorite generating chemicals, but the
15   more common ones are chlorine gas, alkali metal hypochlorites such as sodium hypochlorite, alkaline earth metal hypochlorites such as calcium hypochlorite, chlorinated hydantoins, and chlorinated isocyanuric acid derivatives.
20

Dry sources of biocide are often preferable to gaseous or even liquid forms because the dry forms are often safer to handle, more convenient to store and use, and more stable in storage. Moreover, one or more dry
25   products may conveniently be fed to a recirculating water system using an erosion feeder in which water is passed through a bed of solid biocide to slowly dissolve the biocide and is then added to the recirculating water. One such erosion feeder is described in U.S. Patent 3,412,021.
30

The different forms of hypochlorite donors all work by generating hypochlorous acid (HOCl) in solution, which provides the significant biocidal action. Hypochlorous acid has strong biocidal properties under the proper
35   conditions. Its killing power is adversely affected,

however, by alkaline pH levels and by the presence of
ammonia or other nitrogenous material.

5   The pH of cooling water is typically regulated in the
range of 8.0 to 9.0 for alkaline corrosion protection. At
pH levels above 7.5, chlorine-based biocides become less
effective because of the equilibrium shift from
hypochlorous acid to hypochlorite ion.

10                  $HOCl \rightleftharpoons OCl^- + H^+$ (1)
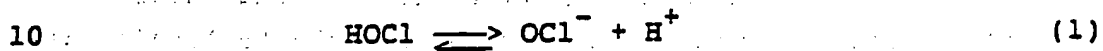
$$pK = - \log\left[\frac{[OCl^-][H^+]}{[HOCl]}\right] = 7.5 \text{ (at } 20°C)$$

15
The hypochlorite ion cannot easily penetrate microorganism
cell membranes, while the uncharged hypochlorous acid can
passively diffuse into cells to cause damage.

20   Water in recirculating water systems is also
frequently contaminated with ammonia due to the
decomposition of nitrogenous impurities in the water or to
the leakage of ammonia from refrigeration units into the
cooling water. Ammonia or chloramines are also commonly
25 introduced into the recirculating water system by the
makeup water. Hypochlorite species react with ammonia to
form chloramines. Since chlorine is bound very strongly
by nitrogen, the chlorine is not readily released by
chloramines to the water as hypochlorite species, and the
30 biocidal activity of the chlorine-based biocide is,
therefore, greatly reduced. The fact that the chloramines
are relatively stable chlorine compounds also makes it
more difficult for some cooling tower systems to comply
with the EPA total halogen (free halogen + combined
35 halogen) discharge limit of 0.2 ppm. In some cases, these
cooling tower systems frequently have to dechlorinate the
discharge water in order to be in compliance. Moreover,
chloramines have a disagreeable and irritating odor. They

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can be converted to odorless nitrogen gas by maintaining
the appropriate free chlorine concentration in the
recirculating water, but some chloramines are still
volatilized into the air. Even though the amounts are
5 negligible, chloramine odors are still noticeable.
Chloramine odor is an important issue with indoor pools
and spas because the air containing the volatilized
chloramines is retained in the buildings long enough for
the chloramine concentration to accumulate to levels that
10 are objectionable to the consumer. Thus, the formation of
chloramines in recirculating water can present a serious
obstacle to the use of chlorine-based biocides.

Hypobromous acid (HOBr), which can be generated from
15 a number of compounds including liquid bromine and N-bromo
organic compounds or by reacting a bromide salt with a
solution of hypochlorous acid or other oxidizing agents,
is a more effective biocide on a molar basis than
hypochlorous acid. Under some conditions, this
20 superiority is quite dramatic. In particular, hypobromous
acid is known to react with ammonia to produce bromamines.
Bromamines, unlike chloramines, have very good biocidal
activity and have a more acceptable odor. Bromamines also
have a distinct advantage over chloramines because they
25 dissipate more readily, thereby making it easier to
operate cooling towers in compliance with the EPA limits
for total halogen. In addition, hypobromite species are
more effective than hypochlorite species at pH values
above 7.5 due to the higher pK value for the equilibrium
30 shift from hypobromous acid to hypobromite ion.

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$$HOBr \; \rightleftharpoons \; OBr^- + H^+ \qquad\qquad (2)$$

$$pK = -\log\left[\frac{[OBr^-][H^+]}{[HOBr]}\right] = 8.5 \;(at\; 20°C)$$

In most cases where hypobromous acid is used as a
biocidal agent, the hypobromous acid generating
composition contains a large weight percentage of bromine.
Liquid bromine, for example, is 100% bromine by weight and
1-bromo-3-chloro-5,5-dimethylhydantoin (BCDMH) is 32.8%
bromine by weight. This practice leads to higher costs
for the bromine-based biocides since the cost of bromine
is about three times the cost of chlorine per pound.
Since 2.25 pounds of bromine contain the same number of
moles of available halogen as only 1.0 pound of chlorine,
bromine is over seven times more expensive than chlorine
on a per mole basis. Even though hypobromous acid is
generally superior to hypochlorous acid, the higher cost
of bromine has limited the use of bromine-based biocides.

Nevertheless, in the past few years several products
have been introduced into the cooling tower marketplace
which take advantage of the bromine chemistry. In 1982,
Nalco introduced a bromine-based product (tradename
Actibrom) for use in large scale cooling towers. These
towers already had chlorinators injecting gaseous chlorine
for disinfection. Actibrom is simply an aqueous solution
of sodium bromide, and is typically added in proportion to
the chlorine gas using a separate feeder. See U.S. Patent
No. 4,451,376. Another bromine-based biocide, 1-bromo-3-
chloro-5,5-dimethylhydantoin (BCDMH) was introduced into
the cooling tower marketplace by Great Lakes Chemical.
See U.S. Patent No. 4,297,224.

Bromine sanitizers have also gained some measure of
popularity for indoor pool and spa applications, because
the odor of the bromamines, formed by reaction of

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hypobromite species with nitrogenous wastes, is less
objectionable to the consumer. Bromine sanitizers,
however, have not been popular for outdoor pools because
the hypobromite species are rapidly dissipated in sunlight
5 and the sanitizer costs are considerably higher than
chlorine sanitizers with cyanuric acid.

Potassium monopersulfate and sodium bromide have been
marketed together as a bromine sanitizer system for spa
10 applications. The recommended practice is to dose the spa
water with sodium bromide (usually as a solution) and then
add the recommended dosages of potassium monopersulfate as
needed. Hypobromous acid is generated by oxidation of the
bromide ion with persulfate ions as shown by the following
15 equation:

$$KHSO_5 \cdot KHSO_4 + NaBr \longrightarrow HOBr + KHSO_4 + NaKSO_4 \qquad (3)$$

Currently available dry sources of hypobromous acid
20 suffer from a number of disadvantages in addition to their
higher cost. The hydantoin products such as BCDMH, 1,3-
dichloro-5,5-dimethylhydantoin (CCDMH), 1,3-dibromo-5,5-
dimethylhydantoin (BBDMH), 1,3-dichloro-5-ethyl-5-
methylhydantoin (CCEMH), and 1-bromo-3-chloro-5-ethyl-5-
25 methylhydantoin (BCEMH) have very low dissolution rates
which necessitates the use of large feeder systems and
high water flow rates. Moreover, in some cases it is
desirable to add a large amount of available halogen at
one time to rapidly clean up a recirculating water system.
30 This is known as a "shock treatment". Such a treatment
would be desired whenever a system has experienced a large
amount of contamination or when microorganism growth has
gotten out of control. However, the hydantoin products
are generally unsuited for this application due to their
35 low dissolution rates.

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In addition, the hydantoin products are not as
effective biocides as might be expected based on the
amount of hypobromous acid formed, because these products
also release large amounts of 5,5-dimethylhydantoin (DMH)
5 or 5-ethyl-5-methylhydantoin (EMH) into the water,
eventually leading to the buildup of high concentrations
of DMH or EMH in the water. High concentrations of DMH or
EMH inhibit the biocidal activity of the hypobromous acid
by virtue of the following equilibria:

10

$$HOBr + DMH \rightleftharpoons H_2O + BDMH \qquad (4)$$

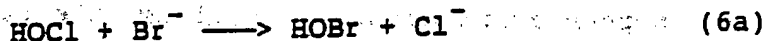$$HOBr + EMH \rightleftharpoons H_2O + BEMH \qquad (5)$$
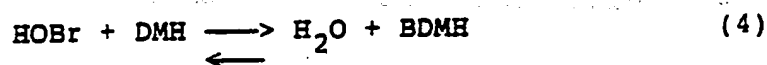
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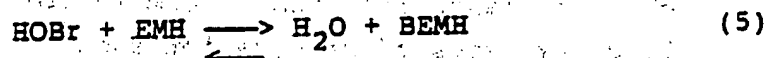
where BDMH is bromo-DMH and BEMH is bromo-EMH. This
effect has previously been noted in U.S. Patent 4,698,165.

As an alternative to the hydantoins, hypobromous acid
20 may be prepared by reacting a bromide salt with a source
of hypochlorite species according to the following
equation:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (6a)$$

25

$$OCl^- + Br^- \rightarrow OBr^- + Cl^- \qquad (6b)$$

as previously taught, for example, in British Patent
1,327,531 and U.S. Patents 2,815,311; 3,975,271; and
30 4,119,535. The hypobromous acid formed by the above
equation is the active biocide. However, in the process
of killing microorganisms or oxidizing organic material,
the hypobromous acid is reduced to form bromide ion, as
shown by the following equation:

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(7)

$$HOBr + microorganisms \longrightarrow dead\ microorganisms + Br^- + H_2O$$
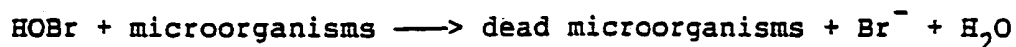
Thus, the bromide ion can be reused to generate more
5   hypobromous acid by reaction with hypochlorite species as
shown above in equations 6a and 6b. Because the bromide
ion is continuously reused, only small amounts of bromide
ion are necessary to make a chlorine-based biocide in
combination with bromide salts perform as a bromine
10 biocide.

Some prior art teaches that, when using mixtures of
chlorine-based biocides in combination with bromide salts
large excesses of bromide ion should be maintained in the
15 recirculating water. For example, British Patent No.
1,327,531 describes a process for sanitizing swimming pool
water wherein the concentration of bromide is maintained
at 20 to 50 mg per liter (expressed as sodium bromide) and
the concentration of the hypobromite species is maintained
20 at 0.4 mg/L. Other prior art, e.g., U.S. Patent No.
3,975,271, suggests that when hypobromous acid is
generated by reacting a bromide salt with a source of
hypochlorous acid, the optimum mole ratio of chlorine to
bromide is near 1. However, no information is provided as
25 to how to maintain the ratio near the optimum in the
recirculating water while chlorine and bromide salts are
being fed simultaneously to the system as well as being
lost from the system.

30   SUMMARY OF THE INVENTION

This invention is broadly concerned with compositions
and methods for controlling biofouling and microorganism
population levels in recirculating water systems using
35 compositions or combinations of hypochlorite donors and
bromide ion donors.

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The proportion of hypochlorite donor and bromide ion
donor in the composition or combination added to the
system is selected to maintain an optimum ratio of all
bromine containing species to the sum of all hypohalite
5 species in the recirculating water. It has now been found
that significant amounts of bromide ion are lost from
recirculating water systems through the pathways of
volatilization of hypobromous acid and bromamines and of
formation of stable organobromine compounds. Moreover,
10 hypochlorite species, hypobromite species, and bromide ion
are lost from the recirculating water at different rates.
These loss rates must be known in order to prescribe at
what rates to feed the hypochlorite donor and bromide ion
donor to the water to compensate for the losses and
15 maintain the desired steady state concentrations.

It is very important, therefore, to control the
chemistries of the reactions of the hypochlorite species
with the bromide ion (equations 6a and 6b) in a dynamic
20 system. More specifically, it is critical to control the
mole ratio of the sum of all bromine-containing species
(HOBr, OBr$^-$ and Br$^-$) to the sum of all hypohalite species
(HOBr, OBr$^-$ HOCl and OCl$^-$) present in the water. For the
purposes of this discussion, this mole ratio will be
25 referred to herein as the "chlorine-to-bromine conversion
ratio" or "Conversion Ratio" ("CR") and will be written
as:

$$CR = \frac{\text{moles of (HOBr + OBr}^- + \text{Br}^-)}{\text{moles of (HOBr + OBr}^- + \text{HOCl + OCl}^-)}$$

30

This ratio will be used hereafter because it is a
convenient way to express the instantaneous measure of the
extent of conversion of the hypochlorite species to
35 hypobromite species. It is also a convenient way to
establish if the hypochlorite donor/bromide ion donor

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compositions are actually performing as a bromine biocide, a mixture of bromine and chlorine biocides, or as a chlorine biocide only. For example, consider the following four scenarios.

5

In the first scenario, the recirculating water does not contain any bromide ion. It follows then that there will be no hypobromite species present. Since the $[Br^-]$ = 0.0 and the $[HOBr]$ = $[OBr^-]$ = 0.0, then hypochlorite

10   species will have some finite values; e.g., 0.5 mole of $HOCl$ and 0.5 mole of OCl^-. Also, CR = 0.0 as shown by the following calculation:

$$CR = \frac{(0.0 + 0.0 + 0.0)}{(0.0 + 0.0 + 0.5 + 0.5)} = \frac{0.0}{1.0} = 0.0$$

15

Under these conditions, the biocide will perform as a chlorine biocide.

20   Assume in the second scenario that the recirculating water contains 0.5 mole of bromide ion, 0.5 mole of $HOCl$ and 0.5 mole of OCl^- before the hypochlorite species/bromide ion reactions occur. Under these conditions, there is only enough bromide ion to satisfy

25   one-half of the stoichiometric requirements of the reactions outlined in equations 6a and 6b. Therefore, essentially all of the bromide ions will be converted to hypobromite species, but only one-half the hypochlorite species will be converted to hypobromite species. Also,

30   one-half the hypochlorite species will still be present. Thus, the hypohalite species in the water will be a 50/50 mixture of hypochlorite species and hypobromite species and the CR will be 0.5 as shown by the following calculation:

35

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$$[HOBr] + [OBr^-] = 0.5 \text{ mole}$$

$$[HOCl] + [OCl^-] = 0.5 \text{ mole}$$

5

$$[Br^-] = 0.0$$

$$CR = \frac{(0.5 + 0.0)}{(0.5 + 0.5)} = \frac{0.5}{1.0} = 0.5$$

10   Since the hypochlorite donor/bromide ion donor
composition is capable of only maintaining a 0.5
Conversion Ratio, it will exhibit biocidal properties
intermediate between that of a chlorine biocide and a
bromine biocide. It follows then that any hypochlorite
15 donor/bromide ion donor composition that maintains a
Conversion Ratio between 0.0 and 1.0, will exhibit the
same properties.

     In the third scenario, assume that there are 1.0 mole
20 of bromide ion and 1.0 mole of hypochlorite species (0.5
mole of HOCl and 0.5 mole OCl$^-$) before the HOCl/Br$^-$ and
OCl$^-$/Br$^-$ reactions occur. Under these circumstances,
essentially all of the hypochlorite species will be
converted to hypobromite species. Similarly, essentially
25 all of the bromide ions will be converted to hypobromite
species. Hence, there will be essentially no hypochlorite
species and bromide ions left. As a consequence, after
the reactions, the Conversion Ratio will be 1.0 as shown
by the following calculation:

30

$$[Br^-] = 0.0$$

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$$[HOCl] = [OCl^-] = 0.0$$

$$[HOBr] + [OBr^-] = 1.0$$

5      $$CR = \frac{(1.0 + 0.0)}{(0.0 + 1.0)} = \frac{1.0}{1.0} = 1.0$$

And, the hypochlorite donor/bromide ion donor composition will perform as a bromide biocide.

10

Finally, in the fourth scenario, assume that the recirculating water contains 1.2 moles of bromide ion and 1.0 mole of hypochlorite species before the hypochlorite species react with the bromide ion. Upon completion of
15 these instantaneous reactions, the recirculating water will contain essentially no hypochlorite species, 1.0 mole of hypobromite species and 0.2 mole of bromide ion. Accordingly, after the reactions, the Conversion Ratio will be 1.2 as shown below:
20

$$[HOCl] = [OCl^-] = 0.0$$

$$[HOBr] + [OBr^-] = 1.0$$

25      $$[Br^-] = 0.2$$

Thus,

     $$CR = \frac{(1.0 + 0.2)}{(1.0 + 0.0)} = \frac{1.2}{1.0} = 1.2$$
30

As a consequence, the hypochlorite donor/bromide ion donor composition will perform as a bromine biocide.

35   Thus, it is desirable to maintain the Conversion Ratio preferably at or slightly above 1.0. However, as

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will be shown later, there are circumstances where other
Conversion Ratios are desirable. Hence, it is preferable
to maintain the Conversion Ratio between about 0.2 and
20.0 and most preferably between 0.5 and 4.0.

5

In order to control the Conversion Ratio to maintain
a small excess of bromide ion, enough bromide ion must be
fed to the water to compensate for any significant losses
of bromine containing species. Bromide ion is, of course,
10 lost from recirculating water systems through blowdown or
turnover. These terms refer to water that is bled from
the system, a practice necessary to keep dissolved solids
from building up to the point where scaling occurs.
However, there has been no recognition in the literature
15 that bromide ion is lost by volatilization of hypobromous
acid and bromamines when combinations of hypochlorite
donors and bromide ion donors are used to generate
hypobromite species. Moreover, the literature contains no
recognition that significant bromide ion losses can occur
20 through the reaction of hypobromite species with organic
materials in the recirculating water. Nor has the
literature recognized the magnitude and the rate of
bromide ion losses that can result from the volatilization
and organobromine compound pathways. More importantly,
25 the literature contains no recognition that knowledge of
the bromide ion loss phenomenon may be used to develop
compositions comprising hypochlorite donors and bromide
ion donors that are capable of simultaneously compensating
for the bromide ion losses and satisfying the chlorine
30 demand of the recirculating water. Without knowledge of
bromide ion loss pathways, as will be shown in the
detailed description of this invention, it is virtually
impossible to develop commercial products that will
perform like bromine-based biocides without using a large
35 excess of bromide ion. Thus, all significant pathways of
bromide ion loss must be accounted for in order to

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maintain an optimum Conversion Ratio in the recirculating water.

The failure of the prior art to adequately compensate for bromide ion loss is evident in the prior art's use of either large excesses of bromide ion or of insufficient amounts to maintain maximum biocidal activity. Any large excess of bromide ion is wasted since it is eventually discarded, for example, in the cooling tower blowdown or pool water turnover. Also, as will be shown in the detailed description of the present invention, a large excess of bromide ion is unnecessary because the physical and chemical dynamics of the recirculating water system will force the bromide ion concentration to a steady state condition. In many cases, this will result in considerable loss of bromide ion. As a consequence, it is preferable and more economical to supply only sufficient bromide ion to the recirculating water to maintain the Conversion Ratio at, or slightly above, 1.0 to ensure maximum biocidal effectiveness.

In one aspect, the present invention provides a biocide composition containing a hypochlorite donor and a bromide ion donor in amounts sufficient to satisfy the chlorine demand of the system and maintain an optimum Conversion Ratio.

In another aspect, the present invention provides a method of treating recirculating water which comprises the steps of ascertaining the rates of bromide ion loss from the system due to blowdown, volatilization, and formation of stable organobromine compounds and adding a hypochlorite donor and a bromide ion donor in amounts sufficient to compensate for the bromide ion losses and maintain an optimum Conversion Ratio.

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Suitable hypochlorite donors include gaseous
chlorine, alkali metal and alkaline earth metal
hypochlorites, chlorinated hydantoins, chlorinated
oxazolidinones, chlorinated imidazolidinones, and
5   chlorinated isocyanuric acid derivatives.

Suitable bromide ion donors include liquid bromine,
bromine chloride, alkali metal and alkaline earth metal
bromides, quaternary ammonium bromides, bromamines,
10   brominated hydantoins, brominated sulfonamides, brominated
succinimides, brominated oxazolidinones, brominated
imidazolidinones, brominated isocyanurates, and salts of
trihalide or mixed trihalide ions containing bromine.

15   In a preferred embodiment the hypochlorite donor and
bromide ion donor are dry solids having a higher
dissolution rate and a higher water solubility than
hydantoins. Preferred dry solids include
trichloroisocyanuric acid or sodium or potassium
20   dichloroisocyanurate and sodium or potassium bromide.
When these compounds are used, it has been found that
proportions of about 85 to about 99 parts by weight
hypochlorite donor and about 1 to about 15 parts by weight
bromide ion donor are capable of maintaining the
25   Conversion Ratio in the optimum range for most water
systems. In other instances, e.g. when hydantoin
derivatives are used as the bromide ion donor, different
proportions are sometimes necessary. For these compounds,
it has been found that proportions of about 50 to about 99
30   parts by weight hypochlorite donor and about 1 to about 50
parts by weight bromide ion donor are capable of
maintaining an optimum Conversion Ratio.

It has now also been found that certain compounds can
35   be added to the recirculating water system to suppress the
loss of bromide ions through volatilization of hypobromous

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acid and bromamine. The bromine volatilization
suppressants may be included in the hypochlorite
donor/bromide ion donor biocide composition or combination
thereof or may be added separately to the recirculating
5 water. Suitable bromine volatilization suppressants
include hydantoin derivatives, sulfonamide derivatives,
sulfamic acid derivatives, glycoluril derivatives,
oxazolidinone derivatives, imidazolidinone derivatives and
succinimide derivatives.
10

Other features and advantages of the present
invention will become apparent from the following detailed
description, which is given by way of illustration only.

15   BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 illustrates the effect of the Conversion
Ratio on killing efficiency.

20   FIGURES 2-6 illustrate the effect of the hypochlorite
donor/bromide ion donor composition on the Conversion
Ratio in the recirculating water and the ability of the
biocide to perform as a bromine biocide. NaBr/ACL90 PLUS
and NaBr/ACL60 compositions are used to illustrate the
25 effects.

FIGURE 7 illustrates the effect of DMH on the Henry's
Law constant for a bromine biocide.

30   DETAILED DESCRIPTION OF THE INVENTION

A hypochlorite donor compound according to the
present invention may be any chlorine containing compound
capable of providing a sufficient amount of hypochlorite
35 species in aqueous solution, including but not limited to
gaseous chlorine, hypochlorite salts such as lithium

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hypochlorite, sodium hypochlorite, or calcium
hypochlorite, chlorinated hydantoins such as
dichlorodimethylhydantoin, or bromochlorodimethyl-
hydantoin, chlorinated oxazolidinones such as 3-chloro-
5 4,4-dimethyl-2-oxazolidinone, chlorinated imidazolidinones
such as 1,3-dichloro-4,4,5,5-tetramethyl-2-
imidazolidinone, or chlorinated isocyanuric acid or its
derivatives including its salts, hydrates, complexes, or
mixtures thereof.
10

Some disadvantages may occur with the use of certain
of these hypochlorite donor compounds. For example,
addition of calcium is not desirable since repeated use
could increase the calcium ion concentration in the water
15 to the level where calcium scaling problems could occur.
Since chlorine gas is a hazardous material, its use is
generally limited to the larger, more sophisticated
recirculating water systems. Finally, many of the
chlorinated organic compounds are less useful than the
20 chlorinated isocyanuric acid derivatives due to higher
costs, lower dissolution rates, lower halogen content,
and/or the buildup of species which inhibit biocidal
activity.

25   Preferred hypochlorite donor compounds include
chlorinated isocyanuric acid derivatives chosen from the
following group of compounds: sodium dichloro-s-
triazinetrione (also called sodium dichloroisocyanurate,
available from Monsanto Co. under the tradename ACL60),
30 potassium dichloro-s-triazinetrione (available from
Monsanto Co. under the tradename ACL59), the hydrate of
sodium dichloro-s-triazinetrione (available from Monsanto
Co. under the tradename ACL56), dichloroisocyanuric acid,
trichloro-s-triazinetrione (also called
35 trichloroisocyanuric acid, available from Monsanto under
the tradename ACL90 PLUS), mixtures thereof such as

[mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-
triazinetrione and [mono(trichloro)-mono(monopotassium
dichloro)]-di-s-triazinetrione. These compounds are
disclosed, for example, in U.S. Patents 3,035,056;
5 3,035,057; 3,150,132; 3,256,199; 3,294,797; and 3,564,146.

The bromide ion donor according to the present
invention may be any compound capable of providing a
sufficient amount of bromide ion in aqueous solution
10 including, but not limited to, liquid bromine, bromine
chloride, alkali metal bromides, alkaline earth metal
bromides, R_4-ammonium bromide where R is an alkyl or aryl
group, bromamines, N-brominated organic compounds, such as
N-brominated hydantoins, N-brominated sulfonamides, N-
15 brominated oxazolidinones, N-brominated imidazolidinones,
N-brominated imides such as N-bromosuccinimide or N-
brominated isocyanurates which can release hypobromite
species or salts of trihalide or mixed trihalide ions such
as Br_3^- or $ClBr_2^-$ as described in U.S. Patent 3,152,073.
20

The hypochlorite donor compound and the bromide ion
donor compound may be added either separately or as a
single composition. For some combinations, the two
components must be added separately, for example, chlorine
25 gas and sodium bromide. In many cases, however, it is
advantageous to premix the two components and add the
compositions to the recirculating water system. This
reduces the number of materials to be handled and thus the
number of controls required. Thus, it is possible to
30 introduce the biocide of the present invention into the
recirculating water system by any of the following means:
an erosion feeder, a floater, porous bags, perforated
buckets or by hand dosing.

35 A preferred product is a solid dry mixture of a
chlorinated isocyanuric acid derivative and a bromide ion

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donor, most preferably compacted in the form of a tablet,
stick or puck. One or more compacting aids such as boric
acid, sodium stearate, potassium stearate, aluminum
hydroxide or monoglycerol stearate may optionally be used.
5 To eliminate any possible interaction between the two
components of the mixture it is necessary to eliminate any
free water, as taught in U.S. Patent 2,815,311. If free
water is present, the two components may react to form
bromine gas, which can corrode metallic containers or pose
10 a health hazard to persons handling the material. In
addition to optional compacting aids, the biocide of the
present invention may also optionally include one or more
scale inhibitor compounds such as polymaleic acid,
polyacrylic acid, a phosphonate, a polyphosphate, or
15 mixtures thereof.

When the product used is a mixture of a solid
hypochlorite donor and a bromide ion donor, the
appropriate composition depends on the operating
20 characteristics of the individual recirculating water
system. Therefore a range of compositions is required
since there are a number of differences between systems.
These differences include variation in the quality of the
water used for makeup, variation in local air quality,
25 variation in the blowdown or turnover rate, and other
system variables. For a composition of
trichloroisocyanuric acid and sodium bromide, the weight
percent of sodium bromide in the composition required to
provide the optimum Conversion Ratio in the recirculating
30 water typically ranges from about 3% NaBr to about 15%
NaBr, depending on how the recirculating water system is
operated.

To maintain the Conversion Ratio in solution at the
35 desired optimum, it is necessary to control both the sum
of the concentrations of the hypohalite species (HOCl,

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OCl^-, HOBr, and OBr^-) and the sum of the concentrations of all bromine containing species (HOBr, OBr^-, and Br^-).

Control of the free halogen concentration is
5   straightforward and is normally achieved for most systems, either with automated analyzer/control equipment or manually with the use of analytical test kits. Test kits and analytical control equipment determine free halogen concentrations by measuring the oxidizing potential of the
10   species dissolved in the water. However, these devices are incapable of distinguishing whether the oxidizing potential was due to hypochlorite or hypobromite species. Consequently, the free halogen concentrations measured in the recirculating water systems are the sum of the free
15   chlorine and the free bromine, and will usually be expressed in terms of free chlorine, since chlorine test kits are more widely used. The free halogen concentrations may also be expressed in terms of free bromine by: (1) multiplying the free chlorine reading by
20   2.25, which is the ratio of the molecular weights of molecular bromine to molecular chlorine (160/71 = 2.25) or (2) using a bromine test kit. However, when the Conversion Ratio in the recirculating water is one or greater, all of the free halogen species will be present
25   as free bromine species, even though the free bromine may be expressed in terms of free chlorine.

Initially, it was believed that bromide ion would be a conserved specie in recirculating water systems, that
30   is, that blowdown or turnover would be the only significant pathway for bromide ion loss. Blowdown or turnover loss, BrL(BD), may be calculated using the following equation, assuming constant bromide ion concentration:
35

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$$BrL(BD) = Q_b \times C_{Br} \times \frac{3.79}{1000} \tag{9}$$

where: $BrL(BD)$ = bromide ion loss due to blowdown, gm/day

Q_b = blowdown or turnover rate, gal/day

C_{Br} = total concentration of all bromine species, mg/liter

3.79 = conversion factor, gallons to liters

1000 = conversion factor, grams to milligrams

Example: a system contains 1.0 mg Br/liter distributed between bromide ion and hypobromite species, and has a blowdown rate of 1000 gal/day. The calculated bromide ion loss due to blowdown would then be 3.79 gm Br/day.

Measurement of the bromide ion concentration during initial experiments has unexpectedly revealed the existence of other significant pathways of bromide ion loss. Further investigation has now demonstrated that in order to maintain an optimum Conversion Ratio, it is necessary to compensate for bromide ion losses by three additional pathways: 1) volatilization of hypobromous acid, 2) volatilization of bromamines and 3) formation of organobromine compounds. Loss of bromide ion by the volatilization of hypobromous acid occurs as a result of the reaction described in equation (6a).

Bromide ion losses via volatilization of bromamines occurs as a consequence of the reaction between hypobromous acid and nitrogenous contaminants (expressed in terms of ammonia).

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$$HOBr + NH_3 \rightarrow BrNH_2 + H_2O \qquad (10)$$
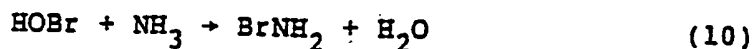
Organobromine compound formation occurs due to the reaction of hypobromous acid with organic matter in the 5 water to form compounds with carbon-bromine bonds, for example:

$$HOBr + R-CH_3 \rightarrow R-CH_2Br + H_2O \qquad (11)$$
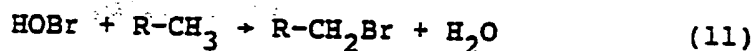
10 The organobromine compounds include the trihalomethanes or other brominated alkanes, brominated carboxylic acids, and the like. The carbon-bromine bonds are very stable and not readily hydrolyzed. Hence, the bromine specie is no longer available as bromide ion for regeneration to 15 hypobromous acid by hypochlorous acid. Therefore, the bromide ion has been effectively removed from this chemical recycle loop.

It is necessary to establish the magnitude of the 20 bromide ion losses by these pathways in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. This can be accomplished by two methods: 1) analytical determination of the decrease in bromide ion 25 concentration ("the bromide ion analytical method") and 2) calculation of losses by the different pathways.

The determination of the appropriate amounts of bromide ion donor and hypochlorite donor can be achieved 30 by the bromide ion analytical method as outlined in the following:

1.   Take samples of the recirculating water at regular intervals and note the sample times.
35

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2. Determine the bromide ion concentration of the water samples with ASTM D-1246-82a, Method D - Ion Selective Electrode For Bromide. Note, in this case, the hypohalite species (HOBr, OBr$^-$, HOCl, OCl$^-$) must be

5 converted to halide species (Cl$^-$ and Br$^-$) prior to the determination of bromide ion. This is achieved by adding sodium sulfite to the solutions in amounts of 1.25 times the stoichiometric amount required to satisfy the following equation:
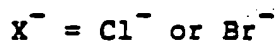
10

$$OX^- + Na_2SO_3 \rightarrow Na_2SO_4 + X^- \qquad (12)$$

where: $OX^- = OCl^-$ or OBr^-

15                $X^- = Cl^-$ or Br^-
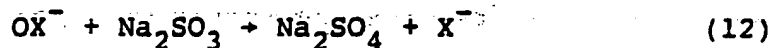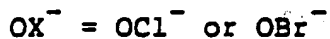
3. Calculate the total daily loss of bromide ion TBrL, in grams per day by using the analytical and sample time data.

20

4. Determine the amount of bromide ion donor, BrD, required to compensate for the losses and maintain the bromide ion concentration at the desired level with the following equation:

25

$$BrD = \frac{M_{BrD} \times TBrL}{M_{Br}} \qquad (13)$$

30 where: BrD = amount of bromide ion donor required to compensate for losses and maintain the bromide ion concentration at the desired level, gm/day

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M_{BrD} = mole weight of bromide ion donor, gm

M_{Br} = mole weight of bromide ion, gm

5   TBrL = total daily bromide ion losses, gm/day

5.   Determine the daily chlorine demand, CD, of the system.

10   6.   Determine the amount of hypochlorite donor compound required to satisfy the daily chlorine demand with the following equation:

$$HCD = \frac{CD}{AvC} \times 100\% \qquad (14)$$

15

where: HCD = amount of hypochlorite donor compound required to satisfy the chlorine demand, gm/day

20

CD = chlorine demand of the system, gm Cl_2/day

AvC = available chlorine content of chlorine donor (wt %)

25

7.   For hypochlorite donor/bromide ion donor combinations where it is more practical to feed the two donors separately, the results of steps 4 and 6 indicate what the feed rates must be for the corresponding donors
30 in order to satisfy the chlorine demand and bromide ion donor requirements and to make the combinations perform as bromine biocides.

8.   For a hypochlorite donor/bromide ion donor
35 combination that will be contained in a single composition or product, a composition is determined by the following calculations:

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a. Hypochlorite Donor/Bromide Ion Donor
    Composition Requirements

$$BGC = HCD + BrD \tag{15}$$

where: BGC = amount of hypochlorite donor/bromide ion
            donor composition required to satisfy the
            chlorine demand and bromide ion
            requirements simultaneously, gm/day

b. Hypochlorite Donor/Bromide Ion
    Donor Composition.

$$\% \text{ hypochlorite donor} = \frac{HCD}{BGC} \times 100\% \tag{16}$$

$$\% \text{ bromide ion donor} = \frac{BrD}{BGC} \times 100\% \tag{17}$$

Although it is an alternative to calculating the
appropriate amounts of bromide ion donor and hypochlorite
donor to feed to the system, the bromide ion analytical
approach is generally beyond the sophistication of most
cooling tower, swimming pool and spa operations or would
require a considerable expense for added instrumentation.

The present invention obviates the need for this
costly instrumentation, since the appropriate amounts of
hypochlorite donor and bromide ion donor may also be
established by the second method, that is, by calculating
bromide ion losses. Investigations relating to the
present invention demonstrate that the bromide ion can be
lost by pathways other than blowdown. At the optimum
Conversion Ratio, the losses incurred by these pathways
can be several times larger than the blowdown loss, making
it virtually impossible to maintain the desired Conversion

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Ratio without knowledge of these pathways. The magnitudes
of the losses by the various pathways are totally
surprising. At Conversion Ratios much higher than
optimum, the percentage of the total bromide ion lost by
5   these pathways is much lower, because the ionic bromide
form is not volatile. In such cases, the volatilization
losses are not readily apparent. Thus, since prior art
use of bromide-based biocides was not at the optimum
Conversion Ratio, the loss of bromide ion by these
10.   pathways was not recognized. Because bromide ion was
usually present in excess, the prior art did not perceive
the importance of these additional bromide ion loss
pathways.

15   The amount of bromide ion lost by flashoff of HOBr,
BrL(FL), may be calculated using either equation (18) or
(19).

$$20 \quad BrL(FL) = \frac{f \times H_k}{W_L/W_G} \times R \times C_{HOBr} \times \frac{M_W}{M_a} \times \frac{M_{Br}}{M_{HOBr}} \times \frac{3.79}{1000} \quad (18)$$

or

$$25 \quad BrL(FL) = fH_kQ_aD_aC_{HOBr} \times \frac{M_W}{M_a} \times \frac{M_{Br}}{M_{HOBr}} \times \frac{28.316}{1000} \times 1440 \quad (19)$$

30   where: BrL(FL) = amount of bromide ion lost by flashoff
                     of hypobromous acid, gm Br/day

              R = the recirculation rate of the
                   recirculating water system, gal/day
35

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f = flashoff equilibrium coefficient for the recirculating water system. (Note, f has a value between 0 and 1.)

5   H_k = Henry's Law Constant for hypobromous acid at the pH and temperature of the recirculating water system

Q_a = the flow rate of air through the

10   tower, $ft^3/min.$

D_a = density of air, gm/L

W_L/W_G = ratio of the mass flow rate of the

15   recirculating water to the mass flow rate of air through the system

M_{HOBr} = mole weight of hypobromous acid, gm

20   C_{HOBr} = the concentration of hypobromite species as hypobromous acid, mg HOBr/L

M_W = mole weight of water, gm

25   M_a = mole weight of air, gm

M_{Br} = mole weight of bromide ion, gm

3.79 = conversion factor, gallons to liters

30   1000 = conversion factor, grams to milligrams

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28.316 = conversion factor, cubic feet to
          liters

1440 = conversion factor, days to minutes
5

It is important to point out that the value of C_{HOBr}, the concentration of hypobromite species, is not the same as C_{Br}, the sum of concentrations of all bromine-containing species, since some of the bromine species
10 present can be in the form of bromide ion.

Henry's Law constant is defined by the following equation:

15                                $C_{solute\ (gas)}$ (20)
                        $H_k = \dfrac{\ }{C_{solute\ (liquid}}$

20 where: H_k = Henry's Law Constant

        $C_{solute\ (gas)}$ = concentration of volatile solute
                                     in the gas phase

25

        $C_{solute\ (liquid)}$ = concentration of volatile solute
                                     in the liquid phase

Henry's Law constant is, therefore, the ratio of the
30 concentration of solute in the vapor phase at equilibrium
     to the concentration of the solute dissolved in a solvent,
     in these cases water. This constant is a measure of the
     tendency of the dissolved solute to escape or volatilize
     from the solvent. A low Henry's Law constant indicates
35 little tendency for the solute to volatilize. A high
     constant value indicates a greater tendency of the solute
     to escape from the solution into the gas phase. Henry's
     Law constants can be expressed in any combination of a
     number of concentration units, such as partial pressure,

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milligrams per liter, or mole fraction. Herein, mole
fraction units are used for both the gas and liquid phase
concentrations.

5   As an example, a cooling tower has W_L/W_G = 1.3, f =
0.5, R = 400,000 gallons/day, and the tower operates at pH
= 8.0 and 30°C. For the conditions in this particular
example, Henry's Law constant is 0.25. The concentration
of free halogen is 0.5 mg/L (0.5 ppm, free chlorine
10   basis). The bromide ion concentration is maintained at
0.8 mg/L (0.8 ppm) to give a Conversion Ratio of 1.05,
slightly greater than the optimum value of 1. Thus, all
of the free halogen species are essentially free bromine
species (HOBr and OBr$^-$). As a result, the free bromine
15   concentration in terms of hypobromous acid is 0.685 mg/L
$[C_{HOBr}$ = FAvC x M_{HOBr}/M_{Cl_2} = 0.5 x 96.9/71 = 0.685].
Under these conditions, the flashoff loss of bromide ion
via the volatilization of hypobromous acid is 51.1 grams
of bromide ion per day. This loss is considerably larger
20   than that due to blowdown (cf. blowdown loss calculation
above), demonstrating that volatilization of hypobromous
acid can be a major factor contributing to the loss of
bromide ion from recirculating water systems.

25   The Henry's Law constant for hypobromous acid used in
the above example was determined as follows, using a pilot
scale cooling tower since there is no literature data for
hypobromous acid or any of the bromamines. The pilot
cooling tower was a counterflow type with a capacity of 80
30   liters of water, which was circulated through the tower at
1.2 gal/min. The air flow rate was 2800 L/min. An
electrical heater, placed in the recirculation line,
provided a constant heat source. In each experiment, the
pilot tower was filled with chlorine-demand-free water and
35   an appropriate amount of biocide was added to give 4.0
mg/L (as chlorine). During the test, the biocide

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concentration was continuously monitored using a Hach CL17
chlorine analyzer. The water was initially recirculated
with no air flow for 30 minutes to establish a baseline
free halogen concentration. The air flow was then started
and the free halogen concentration was monitored for four
hours. The drop in the halogen concentration during this
period, which is due to volatilization of any volatile
species, can be used to calculate the Henry's Law constant
using the following equation:

$$H_k = - \frac{(\log C_f - \log C_i)}{t} \times \frac{2.303 \ V_w \ D_w \ M_a}{Q_a \ D_a \ M_w}$$

where: H_k = Henry's Law constant at temperature and pH
                of the experiment

           V_w = volume of recirculating water, liters

           D_w = density of water, gm/ml

           D_a = density of air, gm/ml

           M_w = mole weight of water, gm

           M_a = mole weight of air, gm

           Q_a = volumetric air flow, L/min

           C_f = final halogen concentration, mg/L

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$$C_i = \text{initial halogen concentration, mg/L}$$

$$t = \text{length of time of experiment, min}$$

5

This procedure assumes that the hypobromous acid has
reached equilibrium between the gas and liquid phases.
With this method, Henry's Law constants were determined
for hypobromous acid as a function of pH, temperature, and
10 the concentration of additional chemical species.

As stated previously, the presence of ammonia in the
recirculating water has also been found to increase the
loss of bromide ion. This is due to the formation of
15 various bromamine compounds, especially monobromamine,
which is more volatile than hypobromous acid. The effect
of ammonia on the volatility of hypobromous acid is
reflected in an increase in the Henry's Law constant.
This change in the Henry's Law constant is dependent on
20 the ratio of ammonia to free bromine, the pH, and the
temperature. There are no literature values for the
Henry's Law constants for bromamines. The results of our
measurements indicate the Henry's Law constant for
bromamines is considerably larger than the Henry's Law
25 constant for hypobromous acid under the same conditions.
The simple bromamines are, therefore, very volatile and do
not build up to significant levels because they are
flashed off very rapidly.

30   Under steady state conditions, the loss of the simple
bromamines by flashoff will be approximately equal to the
rate of formation of monobromamine. The bromamine
formation rate is determined by the rate of introduction
of ammonia into the recirculating water. In most cases,
35 the major source of ammonia is the makeup water. Thus,

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the flashoff loss due to formation of bromamines, BrL(BA),
can simply be estimated by the following equation:

$$BrL(BA) = C_{NH_3} \times Q_m \times \frac{M_{Br}}{M_{NH_3}} \times \frac{3.79}{1000} \qquad (21)$$

where: BrL(BA) = amount of bromide ion lost by flashoff
              of bromamines, gm/day

         C_{NH_3} = concentration of ammonia in makeup
                water, mg/L

         Q_m = makeup water rate, gal/day

         M_{Br} = mole weight of bromide ion, gm

         M_{NH_3} = mole weight of ammonia, gm

         3.79 = conversion factor, gallons to liters

         1000 = conversion factor, grams to
                milligrams

Note, equation (21) applies only to relatively small
ammonia concentrations.

    Another significant pathway for bromide ion loss is
the formation of organobromine compounds as a result of
the reaction of hypobromous acid with organic molecules
dissolved or suspended in the water. Carbon-bromine
covalent bonds are usually stable to hydrolysis so that
the bromine is not released back into the water and is not
available for regeneration to hypobromite species. The
amount of bromide ion loss can vary widely depending on
the organic content of the water, which can be quantified

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as TOC. TOC, or total organic carbon (in mg/L), measures
the total amount of organic material dissolved or
suspended in the water, without distinguishing the
chemical form. Several commercial analyzers are available
5   which perform this analysis. Lab experiments with both
tap water and untreated surface water have shown that
about 0.2 mg/L of bromide ion is combined as organobromine
compounds for every mg/L of TOC introduced into the water.
This number varies somewhat depending on the individual
10   water source, but 0.2 is a reasonable estimate for most
cases.

      The amount of bromide ion loss caused by the
formation of organobromine compounds, BrL(OBr) can be
15   calculated with the following equation, which accounts for
the total organic carbon introduced with the makeup water:

$$BrL(OBr) = Q_m \times 0.2 \times TOC \times \frac{3.79}{1000} \qquad (22)$$

20

where: BrL(OBr) = amount of bromide ion lost due
                               to the formation of
                               organobromine compounds, gm/day

25

                    Q_m = makeup water rate, gal/day

                    TOC = total organic content of makeup
                          water, mg/L

30

                    0.2 = amount of bromide ion lost per
                          mg/L of TOC in recirculating
                          water, mg/L

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3.79 = conversion factor, gallons to liters

1000 = conversion factor, grams to milligrams

Note, equation (22) applies only to relatively small TOC concentrations. This calculation does not account for any TOC added from sources other than makeup, for instance, organic or biological contamination absorbed from the air blown through the tower or contamination from process leaks. If such contamination is severe, the additional loss of bromide ion by reaction with these sources of TOC should also be accounted for.

It is necessary to quantify the major pathways of bromide ion loss, blowdown, flashoff, and organobromine formation in order to determine the appropriate proportions of bromide ion donor and hypochlorite donor to feed to the recirculating water system. Once each of the bromide ion pathway losses are quantified, the optimum proportions of bromide ion donor and hypochlorite donor to be fed to the system may be calculated according to the following steps:

1) Define the desired free halogen concentration (available chlorine basis), FAvC, and the desired Conversion Ratio, CR. CR may range from about 0.2 to about 20.0, more preferably from about 0.2 to about 10.0, and most preferably from about 0.5 to about 4.0. If excess bromide ion is desired CR should be greater than 1.0; if not, then CR can be less than 1.0.

2) Convert the desired free halogen concentration to the concentration of hypobromous acid, C_{HOBr}, by multiplying the free chlorine concentration, FAvC, by 1.37

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x CR if CR is less than 1.0 or by 1.37 if CR is greater
than 1.0. The factor 1.37 is equal to 96.916/70.906
(molecular weight of HOBr/molecular weight of chlorine).

5   3)   Calculate the desired total concentration of all
bromine containing species, C_{Br}, in terms of bromide ion,
using the following equation:

$$C_{Br} = FAvC \times CR \times \frac{M_{Br}}{M_{Cl_2}}$$

10

        4)   Calculate the daily bromide ion loss caused by
blowdown, BrL(BD), with equation (9).

15

        5)   Calculate the daily bromide ion loss incurred by
the flashoff of hypobromous acid, BrL(FL), using either
equation (18) or (19).

20   6)   Calculate the daily bromide ion loss caused by
bromamine flashoff, BrL(BA), with equation (21).

        7)   Calculate the daily bromide ion loss caused by
the formation of organobromine compounds, BrL(OBr), using
25 equation (22).

        8)   Calculate the total daily bromide ion loss,
TBrL, by combining the results of the calculations in
steps 4, 5, 6, and 7.

30

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$$TBrL = BrL(BD)+BrL(FL)+BrL(BA)+BrL(OBr) \qquad (23)$$

9)   Determine the daily quantity of bromide ion
donor required to compensate for bromide ion losses with
equation (13).

10)   Determine the amount of hypochlorite donor
required to satisfy the daily chlorine demand with
equation (14).

11)   For hypochlorite donor/bromide ion donor
combinations where it is more practical to feed the two
donors separately, the results of steps 9 and 10 indicate
what the feed rates must be for the corresponding donors
in order to satisfy the chlorine demand and bromide donor
requirements simultaneously and make the combination
perform as a bromine biocide.

12)   For products containing both the hypochlorite
donor and bromide ion donor as a single composition or
mixture, determine the appropriate composition with
equations (15), (16) and (17).

The effectiveness of the hypochlorite donor/bromide
ion donor biocides and the bromine volatilization
suppressants disclosed herein is demonstrated in the
following examples, including killing efficiency
experiments, cooling tower and spa tests, and calculations
in which compositions representative of the present
invention, such as ACL60/NaBr and ACL90 PLUS/NaBr, are
compared with chlorine (ACL60) and competitive bromine
(BCDMH) biocides.

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Example 1 - Effectiveness of Hypochlorite Donor/Bromide
Ion Donor Compositions In Cooling Towers

5   A small crossflow, induced draft cooling tower, used
    to cool a 250 ton air conditioning system, was used to
    test the relative effectiveness of the current invention
    versus chlorine and BCDMH biocides over a period of five
    months. The pH of the tower water was controlled at 8.5
10 and the free halogen concentration was controlled at 0.5
    mg/L (available chlorine base) with an automated chlorine
    analyzer/controller. Scale and corrosion inhibitors were
    also added as part of the normal operation of the cooling
    tower. The effectiveness of each biocide was judged on
15 the ability of the biocide to control the biofouling
    microorganism population as measured by a standard plate
    count method. Microorganism populations were reported as
    colony forming units per milliliter (CFU/ml). Samples for
    the determination of microorganism populations and bromide
20 ion concentration were taken from the same location in the
    cooling tower basin away from the point of chemical
    addition. Two to three samples were taken per day.
    Immediately after sampling, any hypohalite species were
    reduced to halide species with sodium thiosulfate. The
25 bromide ion concentration was measured by ion
    chromatography. The results of the test are shown below
    in Table 1:

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TABLE 1

Results of Cooling Tower Biofouling Control Tests
Comparing Biocidal Effectiveness of Hypochlorite
Donor/Bromide Ion Donor Biocide Compositions to Chlorine
and Bromine Biocides.

Biocide Tested	Total Br Conc (mg/L)	Plate Count (CFU/ml)	Conversion Ratio
ACL60	0.0	14,200	0.0
ACL60/NaBr	0.14	5,600	0.25
ACL90 PLUS/NaBr	1.8	4,200	3.2
BCDMH	23.2	24,600	41.1
ACL60/NaBr	18.	1,600	31.9
ACL90 PLUS/NaBr	6.5	1,200	11.5

Notes:

1.   Results are the average values observed during the
test periods.   2.   Test Conditions: pH = 8.5; free
halogen = 0.5 mg/L, available chlorine basis.

In these tests, ACL60 (sodium dichloroisocyanurate)
was used to demonstrate the biocidal effectiveness of
chlorine biocides under these conditions. Combinations of
sodium bromide with ACL60 and sodium bromide with ACL90
PLUS (trichloroisocyanurate) were employed to illustrate
the effect of the Conversion Ratio on the biocidal
effectiveness of the hypochlorite donor/bromide ion donor
compositions, which are representative of the present
invention, and their ability to perform as bromine
biocides. BCDMH was also included to compare the
effectiveness of this bromine biocide to the ones
representative of the present invention.

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The results of these tests show that the hypochlorite donor/bromide ion donor compositions of NaBr/ACL60 and ACL90 PLUS/NaBr, were not only superior to the chlorine biocide, ACL60, but were also superior to the bromine biocide, BCDMH, in controlling the population of the biofouling microorganisms. The most effective NaBr/ACL60 and NaBr/ACL90 PLUS biocide compositions were those which maintained the Conversion Ratio in the recirculating water above 1.

The biocide compositions that were less effective were those which produced Conversion Ratios of less than one. However, all of the NaBr/ACL compositions were more effective than the chlorine (ACL60) and BCDMH biocides, as evidenced by the fact that they controlled the biofouling microorganism population at or below 6000 CFU/ml, whereas the chlorine and BCDMH biocides were not capable of reducing the biofouling populations below 14,000 and 24,000 CFU/ml, respectively, at the same free halogen concentration.

Example 2 - Effectiveness of Hypochlorite Donor/Bromide Ion Donor Biocide Compositions in Biofouling Control Experiments.

The killing efficiencies of the biocides evaluated in Example 1 were also determined in laboratory experiments designed to simulate cooling tower conditions. In these experiments, a culture of microorganisms from the cooling water in Example 1 were cultured in a well-stirred vessel by metering nutrient solution into the solution containing the culture. The vessel contents were maintained at 37°C and pH of 8.0. Each experiment consisted of shocking the microorganisms with the biocide to be tested. Nutrient solution was also fed continuously to the vessel to

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encourage growth of the microorganisms and biocide
solution was fed to the vessel to control the free halogen
concentration at 0.5 mg/L (available chlorine basis) and
the microorganism population. The microorganism
5 population was determined periodically by an HMB-II
apparatus (KVM Engineering) until the microorganism
population had ceased to decline and remained constant for
several hours. This usually occurred in about four hours
after the start of the experiment. At this point, the
10 microorganism growth rate and the microorganism death rate
due to the biocidal activity of the biocide were
considered to be in dynamic equilibrium, or at steady
state. The effectiveness of biocide was then judged on
the basis of killing efficiency as defined by the
15 following expression.

$$KE = \frac{[P_i - P_f]}{P_i} \times 100\% \qquad\qquad (24)$$

20 where: KE = killing efficiency of the biocide, %

P_i = microorganism population at the start of
the experiment, CFU/ml

25   P_f = microorganism population at steady state
conditions, CFU/ml

The results of the biocide killing efficiency experiments
are summarized in Table 2.

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TABLE 2

Results of Biocide Killing Efficiency Experiments

Biocide Tested	NaBr/ACL 60 Wt. Ratio	CR	P_i (CFU/ml)	P_f (CFU/ml)	KE
BCDMH	-.-	-.-	2,140,000	1,260,000	41
ACL60	0.0	0.0	1,560,000	880,000	44
ACL60/NaBr	0.1	0.13	1,960,000	830,000	58
ACL60/NaBr	0.19	0.22	1,410,000	350,000	75
ACL60/NaBr	1.0	1.20	1,460,000	165,000	89

Conditions: pH = 8.5, temperature = 37° C, free
halogen = 0.5 mg/L (available chlorine basis).

The results in Table 2 show that the NaBr/ACL60
compositions (hypobromous acid generating compositions)
have superior biocidal activity relative to the chlorine
biocide, ACL60, and the bromine biocide, BCDMH, under the
conditions of the experiments. The results also support
the validity of the results obtained in the cooling tower
tests (Example 1). The above results also show that the
best killing efficiency was obtained at a Conversion Ratio
of 1.20. This represents the condition where the amount
of NaBr is sufficient to make the bromide ion
concentration in the water slightly in excess of the
stoichiometric amount required to satisfy the reactions
shown in equations (6a) and (6b). Thus, the best killing
efficiency was obtained with the composition that
performed as a true bromine biocide. However, the results
of the experiments indicate that the killing efficiencies
of NaBr/ACL60 compositions which yield Conversion Ratios
of less than 1 are still better than the chlorine (ACL60)
or BCDMH biocides.

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The effect of the Conversion Ratio can be understood
more clearly by referring to the graph shown in Figure 1.
Figure 1 is a plot of the killing efficiency of each
ACL60/NaBr composition tested as a function of the
5   Conversion Ratio. The results show that killing
efficiencies increase as the Conversion Ratios increase
until the maximum killing efficiency is attained near a
Conversion Ratio of 1.0. At this point, all of the free
halogen species are free bromine species. Figure 1 also
10 shows that most of the improvement in killing efficiency
(from 42% to 75%) occurred between Conversion Ratios of
0.0 and 0.2. This indicates that the Conversion Ratio in
the recirculating water system does not have to be
controlled tightly in order for the bromine based biocide
15 to be significantly better than chlorine biocides at pH
levels of 8 or higher.

Even though the performance of the hypochlorite
donor/bromide ion donor biocide will be very good at these
20 low ratios, it is desirable to use these biocides at
Conversion Ratios of 1.0 or more, because the biocides
will control the microorganisms more effectively, thereby
reducing biocide usage, and because the formation of
chloramines will be minimized. Figure 1 shows at what
25 levels the Conversion Ratio should be maintained to obtain
maximum biocidal activity. However, it would not be
economical, in most instances, to use products with
proportions of bromide ion donor and hypochlorite donor
equivalent to the desired Conversion Ratio in the
30 recirculating water. Therefore, it is important to
understand how to develop compositions and methods that
allow hypochlorite donor/bromide ion donor compositions
with low bromide ion donor contents to maintain the
desired Conversion Ratio in the recirculating water.
35

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Example 3 - Discovery of Bromide Ion Loss Phenomenon

During tests run on the cooling tower system
described in Example 1, ACL90 PLUS (trichloroisocyanurate)
5   was fed to the recirculating water system at a rate
sufficient to maintain a free halogen concentration of 0.5
mg/L (0.5 ppm, free chlorine basis). The chlorine demand
of the recirculating water system was determined to be
about 282 grams of available chlorine per day. Since
10   ACL90 PLUS, which has an available chlorine content of
90.7%, was used as the hypochlorite donor, the ACL90 PLUS
requirement was 310.4 grams/day [(282 ÷ 0.907) x 100%].
Sodium bromide was fed to the system at a rate of 2.6 gm
NaBr/day, a rate calculated to account for blowdown loss
15   and maintain a bromide ion concentration of 0.56 mg/L, a
concentration sufficient to maintain a Conversion Ratio of
one. Analyses of water samples taken from the system
revealed, however, that the bromide ion was consistently
as low as about 0.05 mg/L, considerably below the desired
20   bromide ion concentration of 0.56 mg/L. Therefore, the
bromide ion was lost at a rate much higher than expected.

Example 4 - Demonstration of the Bromide Ion Loss
Phenomenon
25

Tests were conducted in the following manner. The
blowdown value for the recirculating water system of the
cooling tower cited in Example 1 was closed to prevent the
loss of water by this pathway. The recirculating water
30   system was then dosed with enough sodium bromide to obtain
a concentration of about 0.5 mg/L (0.5 ppm) of bromide
ion. The free halogen was maintained at 0.5 mg/L (0.5
ppm, free chlorine basis). The water was then
recirculated for about one hour to obtain a uniform
35   concentration of bromide ion throughout the system. Water
samples were then taken periodically over a 24 hour period

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and analyzed for bromide ion. The results of the analyses
in Table 3 show that about 70% of the bromide ions were
lost during this 24 hour period. Loss rates for the first
few hours were actually even higher. For instance, the
5 loss rate for the first 8.5 hours is over 6% per hour or
152% per day.

TABLE 3

10   Bromide Loss Data for Zero Blowdown

Water Sample	Time (hr)	Bromide Ion Conc (ppm)	Bromide Ion Losses (%)	Lithium Conc (ppm)
1	0.0	0.50	0.0	0.42
2	8.5	0.20	54.0	0.40
3	24.0	0.13	69.0	0.41

20   To prove that the bromide ion losses were not due to
leaks in the recirculating water system, the water was
also spiked with lithium chloride at the start of this
test. Lithium is not commonly found in water, can be
easily analyzed for, and is not volatilized from the water
25 system. The water samples taken for bromide analyses were
also analyzed for lithium. The results shown in Table 3
demonstrate that lithium was not lost from the system
during the test, thereby demonstrating that the bromide
ion losses were not due to leaks, but, instead were due to
30 other phenomena.

     This example also demonstrates that the bromide ion
losses can be significant in recirculating water systems,
a fact not recognized by the prior art. In addition, it
35 shows that many of the compositions described in the prior
art for mixtures of hypochlorite donors and bromide ion
donors actually performed as chlorine biocides instead of
performing as bromine biocides like the claimed
compositions. Furthermore, the results clearly indicate
40 that without the knowledge of these losses, it would be

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impossible to make hypochlorite donor/bromide ion donor
compositions which would perform efficiently and
economically as bromine biocides.

5   Example 5 - Compensation for Bromide Ion Loss

        This example demonstrates that with knowledge of the
existence of the bromide ion loss phenomena, bromide ion
losses can be adequately compensated for to produce the
10 desired results -- performance of hypochlorite
donor/bromide ion donor composition as bromine biocides.
As shown in Example 3, prior to the discovery of the
bromide ion loss phenomena, the sodium bromide was fed to
the cooling water system at the rate of 2.6 grams/day, an
15 amount only sufficient to maintain a Conversion Ratio of
0.1 (0.05 ppm divided by 0.5 ppm free chlorine), far below
the ratio required to make the free halogen species
perform as a bromine biocide.

20   The results in Examples 3 and 4 indicated that the
estimated sodium bromide feed rate had to be considerably
higher than the original rate (2.6 grams/day) in order to
maintain a Conversion Ratio of approximately one. Tests
showed that a sodium bromide feed rate of 15-17 grams/day
25 maintained the desired bromide ion concentration.
Furthermore, the biocidal system performed as bromine
biocide as evidenced by the reduction in biofouling
organism population from 14,000 CFU/ml for the 0.01
Conversion Ratio in Example 3 to 5000 CFU/ml.

30

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Example 6 - Determination of Appropriate Hypochlorite
        Donor/Bromide Ion Donor Biocide Composition by
        the Bromide Ion Analytical Method.

5   The following is an example of how this method can be
applied to the determination of the appropriate
hypochlorite donor compound/bromide ion donor composition
for this cooing tower system.

10   In Example 5, the bromide ion donor (sodium bromide)
requirement was determined to be 15.0-17.0 gm/day in order
to maintain the bromide ion concentration at the level
necessary to make the biocide perform as a bromine
biocide. The hypochlorite donor/bromine ion donor
15 composition requirement, BGC, for this particular
combination was 327.4 grams/day (310.4 + 17.0).
Therefore, the appropriate composition was 94.8% ACL90
PLUS [(310.4 ÷ 327.4) x 100%)] and 5.2% [(17.0 ÷ 327.4) x
100%] sodium bromide.

20

        If it is desired to add these two donors as a single
product, the ACL90 PLUS and sodium bromide may be blended
together, compacted into tablets, placed in an appropriate
erosion feeder, and used to satisfy the chlorine demand
25 and bromide ion requirements of the system. The
composition would perform in the above described system as
a bromine biocide. If it is desired to add the ACL90 PLUS
and sodium bromide separately, the feed rates would be
310.4 and 17.0 gm/day respectively.

30

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Example 7 - Bromide Ion Loss and Composition Calculations
for Cooling Towers.

An example of the procedure outlined above for
5 calculating the total bromide ion loss and the
hypochlorite donor/bromide ion donor composition required
to maintain the optimum Conversion Ration is given below.
Three cooling towers, having the characteristics given in
Table 4A, will be used. The three towers are various
10 sizes and have somewhat different operating
characteristics. A major difference between the three
towers is the quality of the makeup water, which has a
significant impact on the amount of bromide ion loss.

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<u>TABLE 4A</u>

Characteristics of Model Cooling Towers

5 Characteristic	Tower A	Tower B	Tower C
Blowdown Rate, Q_b (gal/day)	1,000	2,000	12,000
10 Recirculation Rate, R (gal/day)	200,000	600,000	1.5×10^7
Makeup Rate, Q_m (gal/day)	5,000	10,000	63,000
Desired Free Halogen Conc., FAvC 15 (mg/L, as chlorine)	0.3	0.2	0.1
Desired Conversion Ratio, CR	1.1	0.9	1.2
Flashoff Equilibrium Coefficient, f 20	0.5	0.5	0.5
W_L/W_G	1.3	1.3	3.0
Tower-Top Temperature (°C)	30	30	30
25 pH	8.0	8.0	8.0
Ammonia Concentration in Makeup Water (mg NH_3/L)	0.0	0.1	0.1
30 TOC Concentration in Makeup Water (mg TOC/L)	2.0	1.0	1.0
Biocide Usage (grams ACL90 PLUS/day)	400	700	3,300

35 From the characteristics in Table 4A, the following
parameters can be found for the three example towers.
Sodium bromide (mol.wt. = 102.90 gm/mole) is used as the
bromide ion donor and ACL90 PLUS is the hypochlorite
40 donor.

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TABLE 1B

Calculated Parameters of Model Cooling Towers

Calculated Parameter	Tower A	Tower B	Tower C
HOBr Concentration, C_{HOBr} (mg/L)	0.410	0.246	0.137
Total Br Conc, C_{Br} (mg/L)	0.372	0.203	0.135
Henry's Law Constant, H_k	0.250	0.250	0.250
Blowdown Loss, BrL(BD), grams Br/day	1.41	1.54	6.15
HOBr Flashoff Loss, BrL(FL), grams Br/day	15.30	27.54	165.75
Bromamine Flashoff Loss, BrL(BA), grams Br/day	0.0	17.78	112.01
Organobromine Compound Formation Loss, BrL(OBr), grams Br/day	7.58	7.58	47.75
Total Bromide Ion Loss, TBrL, grams Br/day	24.29	54.44	331.67
Total NaBr Needed, grams/day	31.28	70.10	427.09
% NaBr Needed in ACL90 PLUS/ NaBr Composition	7.25	9.10	11.46

The above calculations show that the flashoff losses can
be much larger than the blowdown loss, especially when
ammonia is present. Given the values above, the
appropriate composition of a trichloroisocyanuric
acid/NaBr mixture is calculated to be 7.25% NaBr for Tower
A, 9.10% NaBr for Tower B and 11.46% NaBr for Tower C. If
the flashoff losses and the loss due to formation of
organobromine species are not accounted for, the
appropriate composition would mistakenly be calculated as
only 0.35% NaBr for Tower A, 0.22% NaBr for Tower B and
0.19% for Tower C.

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   If chlorine gas is being used as the hypochlorite
donor, then the second to last line in Table 4B gives the
amount of sodium bromide that must be added separately to
maintain the optimum Conversion Ratio in the recirculating
5 water.

   Example 8 - Determination of an Appropriate Hypochlorite
              Donor/Bromide Ion Donor Biocide Composition.

10   This example demonstrates why understanding of
bromide ion loss phenomena is critical to development of
commercial biocides containing both hypochlorite donors
and bromide ion donors.

15   In this example, a cooling tower system with a
recirculating water capacity of 100,000 gallons is treated
with ACL90 PLUS to maintain a free available chlorine
concentration of 0.5 mg/L (0.5 ppm) in the water. The
daily available chlorine demand is satisfied with 11.0
20 pounds of ACL90 PLUS. Since the available chlorine
content of ACL90 PLUS is 90.7%, 11.0 pounds of ACL90 PLUS
tablets per day are equivalent to 10.0 pounds of available
chlorine (11.0 x 0.907 = 10.0).

25   The ACL90 PLUS chlorine biocide can be made to
perform as a bromine biocide by adding sufficient sodium
bromide to the water to maintain a Conversion Ratio of at
least 1.0. This requires maintenance of a bromide ion
concentration in the cooling water sufficient to satisfy
30 the stoichiometric requirements of equations (6a) and
(6b). Hence, the bromide ion concentration must be 0.56
ppm (0.5 ppm of Cl_2 x M_{Br}/M_{Cl_2} = 0.5 x 79.909/70.906 =
0.56). Since the recirculating water in the example
cooling tower weighs 834,000 pounds (100,000 gallons x
35 8.34 pounds/gallon), it must contain at least 0.47 pounds
of bromide ion (0.56 x 10^{-6} x 834,000 pounds = 0.47

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pounds). This requires that the water contain a minimum of 0.605 pound of sodium bromide (0.47 pound x M_{NaBr}/M_{Br} = 0.47 x $102.90/79.909 = 0.605$).

5   To make an ACL90 PLUS/NaBr composition perform as a bromine biocide, the composition must contain sufficient sodium bromide to build the bromide ion concentration up to and maintain it at the level required to satisfy the optimum Conversion Ratio. This can be achieved by knowing
10   the bromide ion loss rates for the recirculating water system. If the ACL90 PLUS/NaBr product contains the exact amount of sodium bromide to compensate for the losses and maintain the Conversion Ratio at exactly one, then the sodium bromide concentration will automatically change
15   with time until the desired concentration is reached. This occurs as follows:

When feeding a NaBr/ACL composition to a tower which initially contains no bromide ion, the bromide ion
20   concentration will increase. The bromide ion loss rate depends on the concentration, so that the loss rate at low concentrations is very small, but slowly increases as the concentration of bromide ion increases. Thus, the initial bromide ion addition rate is larger than the bromide ion
25   loss rate and the bromide ion concentration increases. This continues until the bromide ion loss rate matches the rate at which bromide ion is added to the system. At this point, a dynamic equilibrium condition, commonly referred to as a steady state, has been reached. Under these
30   conditions, the bromide ion loss rate is equal to the rate at which bromide ion is being added and no further change in the bromide ion content occurs. If the hypochlorite donor/bromide ion donor composition contained the exact amount of bromide ion to compensate for bromide ion losses
35   at the desired steady state, that is the steady state which is eventually attained.

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On the other hand, if the tower initially contains an excess of NaBr over the amount required for a Conversion Ratio of 1.0 and a NaBr/ACL mixture is used that corresponds to the desired steady state concentration, the
5   bromide ion loss rate will be higher than the bromide addition rate. In this case, the bromide ion concentration will decrease until the loss rate and addition rate are equal and a steady state at Conversion Ratio = 1.0 is reached. Again, this steady state is
10 determined by the bromide ion addition rate, and, if the correct composition is used, the Conversion Ratio will be one at steady state.

This concept can best be visualized by considering
15 the following information. First, in the preceding Example, 11.0 pounds of ACL90 PLUS are required to satisfy the daily chlorine demand of the cooling water. Second, 0.605 lb of sodium bromide are required to maintain the desired Conversion Ratio of 1.0. It follows that the
20 total daily requirements for the hypochlorite donor/bromide ion donor composition, (ACL 90 PLUS/NaBr) are 11.605 pounds (11.0 + 0.605). The appropriate composition of the hypochlorite donor/bromide ion donor composition required to maintain the desired Conversion
25 Ratio is, therefore, 94.8% (11.0/11.605 x 100% = 94.8%) ACL90 PLUS and 5.2% (0.605/11.605 x 100% = 5.2%) NaBr.

To understand how this composition can build up the bromide ion concentration to the desired level, it is
30 necessary to consider the bromide ion addition rate and total bromide ion loss rate on an hourly basis. Again, as shown above, the total weight of bromide ion, W_{Br}, required to maintain the Conversion Ratio at 1.0 was established to be 0.47 lb at steady state. For the
35 purpose of this Example, it is assumed that this will be the total amount of bromide ion that is lost daily. Then

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the total hourly bromide ion loss rate (all pathways),
HTBrL, is simply W_{Br} divided by 24 hours. This
corresponds to a rate of 0.01958 lb/hr (0.47 lb ÷ 24 hr =
0.01958). With respect to W_{Br}, the percent total hourly
5 bromide ion loss rate, PHTBrL is, as determined by
equation (25), 4.2% (0.01958/0.47 x 100% = 4.2%).

$$PHTBrL = \frac{HTBrL}{W_{Br}} \times 100\% \qquad (25)$$

10

This percent total hourly loss rate corresponds to a
percent total daily loss rate of 100%. It is important to
remember that it is entirely possible for percent total
15 daily loss rate to be greater than 100%.

With regards to the bromide ion addition rate, it was
established previously that 0.605 lb of sodium bromide are
required to satisfy the Conversion Ratio conditions
20 specified. The hourly sodium bromide addition rate is
thus 0.02521 lb/hr (0.605 lb ÷ 24 hr). In terms of
bromide ion, the total hourly addition rate is 0.01958
lb/hr (0.02521 lb NaBr/hr x M_{Br}/M_{NaBr} = 0.02521 x 80/103 =
0.01958).

25

It follows that at the end of the first hour of use
of the ACL90 PLUS/NaBr composition the bromide ion content
of the water will be 0.01958 pounds minus the amount of
bromide ion losses. Since the total hourly loss rate is
30 4.2%/hr, the amount of bromide ion lost in the first hour
is only 0.00082 lb (0.042 x 0.01958). The bromide ion
content at the end of the first hour is thus 0.01876 lb
(0.01958 - 0.00082). At the end of the second hour,
another 0.01958 lb of bromide will have been added
35 bringing the gross amount to 0.03834 (0.01876 + 0.01958)
lb. However, the bromide ion loss is slightly higher and
amounts to approximately 0.00161 lb (0.03834 x 0.0420).

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The net amount of bromide ion remaining has now increased
to 0.03673 lb (0.03834 - 0.00161). Thus, with each
successive addition of sodium bromide, the bromide ion
concentration will continue to increase, but at the same
5 time, the bromide ion loss rate will increase.
Eventually, the loss rate will catch up with the addition
rate and the two rates will be essentially equivalent
thereafter. At this point, steady state conditions have
been attained and subsequent ACL90 PLUS/NaBr additions
10 merely maintain the Conversion Ratio at the desired level,
in this case, 1.0

A further refinement of these calculations is to
determine the hourly bromide ion losses by the various
15 pathways, since blowdown losses apply to all bromine
species but losses by flashoff of hypobromous acid and
bromamines and the formation of organobromine compounds
apply only to the hypobromite species. This is achieved
with equations (26) and (27). The percent hourly bromide
20 ion loss rate by blowdown, PHBrL(BD), is calculated by
equation (26).

$$PHBrL(BD) \quad = \quad \frac{BrL(BD)}{C_{Br} \times V_w} \times \frac{1000}{24} \times 100\% \qquad (26)$$

25

where: PHBrL(BD) = the percent of bromide ion lost by
blowdown, %/hr

BrL(BD) = as defined in equation (9)
30

C_{Br} = as defined in step (3) of
"calculation of losses method"

V_w = volume of recirculating water, L
35

1000 = conversion factor, grams to
milligrams

24 = conversion factor, days to hours
40

The percent hourly loss of bromide ion by the other
pathways (flashoff of hypobromous acid and bromamines and

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formation of organobromine compounds) is specifically
proportional to the amount of hypobromite species in the
recirculating water. The percent hourly loss of
hypobromite species by these pathways, PHOBrL, is
5 calculated with equation (27).

$$
\text{PHOBrL} = \frac{[\text{TBrL} - \text{BrL(BD)}]}{C_{\text{HOBr}} \times V_w} \times \frac{M_{\text{HOBr}}}{M_{\text{Br}}} \times \frac{1000}{24} \times 100\% \qquad (27)
$$

where: PHOBrL = percent of hypobromite species lost by
                 pathways other than blowdown, %/hr

15   TBrL = as defined in equation (23)

     BrL(BD) = as defined in equation (9)

      C_{HOBr} = as defined in step (2) of "calculation
20   of losses method"

      V_w = volume of recirculating water, L

      M_{HOBr} = mole weight of hypobromous acid, gm
25
      M_{Br} = mole weight of bromide ion, gm

      1000 = conversion factor, grams to milligrams

30   24 = conversion factor, days to hours

PHOBrL is essentially the weight of hypobromite species
lost per hour divided by the weight of hypobromite species
contained in the recirculating water. With equation (25),
35 the percent total hourly bromide ion loss rate, PHTBrL,
was calculated to be 4.2%/hr. These refinements account
for what fraction of bromide ion losses are due to
blowdown and the other pathways. To illustrate the
refinements of the calculations, the losses due to
40 blowdown, PHBrL(BD), and the losses by other pathways,
PHOBrL, are taken to be 0.83%/hr and 3.33%/hr,
respectively, for Figures 2-5.

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These calculations can be used to illustrate the
interrelationship between the concentration of the bromide
ion in the recirculating water and the composition of the
hypochlorite donor/bromide ion donor compositions. They
5   were utilized to generate the graphs shown in Figures 2-5
which illustrate the effect of the biocide composition on
the buildup of bromide ion with time and the ability of
the composition to attain the optimum Conversion Ratio at
steady state conditions. Since these calculations
10   simulate the dynamics of the bromide ion content of water
recirculation systems, they can be used to determine the
composition required to produce the desired Conversion
Ratio once the PHBrL(BD) and PHOBrL have been determined.
Figure 6 illustrates the effect of bromide ion loss rate
15   on the composition required for the preferred range of
Conversion Ratios. Therefore, it illustrates, in
conjunction with the following examples, how the various
compositions are able to perform as bromine biocides.

20

Example 9 - Buildup of Bromide Ion to Steady State
Concentration with a 2% NaBr/98% ACL90 PLUS Composition.

The cooling tower in Example 8 is initially treated
25   with 11.0 pounds of ACL90 PLUS per day to maintain a free
chlorine concentration of 0.5 mg/L, thus the tower
initially contains no bromine containing species. The
biocide is then switched to a composition of 2% NaBr and
98% ACL90 PLUS. Figure 2 presents the calculated bromide
30   ion content in terms of sodium bromide of the tower versus
the time elapsed since starting the NaBr/ACL90 PLUS
composition, given that PHOBrL = 3.33%/hour (80%/day) and
that PHBrL(BD) = 0.83%/hour (20%/day). It shows how the
total amount of bromine containing species (given as
35   pounds of NaBr) contained in the recirculating water
system builds up with time during the initial few days of

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use of the 2.0% NaBr/98% ACL90 PLUS composition until a
steady state concentration is reached after about three
days. At steady state, the tower in Figure 2 contains
about 0.2 pounds of NaBr, which is considerably below the
5   0.605 pounds of NaBr required for a Conversion Ratio of
1.0, as shown by the line labeled "CR = 1.0". In this
case, the free halogen is a mixture of hypochlorite
species and hypobromite species and the killing efficiency
is less than ideal.
10
Example 10 - Buildup of Bromide Ion to Steady State
Concentration with a 9% NaBr/91% ACL90 PLUS composition.

Figure 3 shows the case where a
15 NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition
with a much higher percentage of NaBr (9.0%) is fed into
the tower described in Example 8. As in Example 9, the
bromide ion content of the tower builds up smoothly until
a steady state is reached. In this case, however, steady
20 state is reached in about 20 days. The steady state NaBr
content is 3.0 pounds and the steady state Conversion
Ratio is 5.0. In this case, all of the free halogen is
present as hypobromite species and the killing efficiency
is very high, but a considerable excess of bromide ion is
25 present which is wasted.

Example 11 - Buildup of Bromide Ion to Steady State
Concentration with the Optimum 5.2%
NaBr/94.8% ACL90 PLUS Composition.

30
Figure 4 shows the ideal case for the tower described
in Example 8, where PHBrL(BD) is 0.83%/hour (20%/day) and
PHOBrL is 3.33%/hour (80%/day). A Conversion Ratio of 1.0
is achieved after about three days and then maintained at
35 steady state conditions by feeding a composition of 5.2%
NaBr/94.8% trichloroisocyanuric acid. This composition

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therefore performs as a bromine biocide in this tower with
very little excess bromide ion being required.

Example 12 - Buildup of Bromide Ion to Steady State
Concentration with BCDMH

Figure 5 shows the case for BCDMH, which has a
bromide and available halogen content equivalent to about
40% NaBr/60% trichloroisocyanuric acid, in the tower of
Example 8. The steady state Conversion Ratio (for PHOBrL
= 3.33%/hour and PHBrL(BD) = 0.83%/hour) which is attained
after about 20 days is 56.7. This is a tremendous waste
of bromide ion, since 56.7 times as much bromide is used
as is necessary to maintain the maximum killing
efficiency. This high Conversion Ratio for BCDMH is
confirmed by the data in Example 1, Table 1, where a
Conversion Ratio of 41.1 was determined experimentally for
BCDMH in a tower with somewhat different characteristics.
The waste of bromide is even greater for cases where
PHOBrL and PHBrL(BD) are lower than used in this example.

Example 13 - Hypochlorite Donor/Bromide Ion Donor
Compositions Required For Specific Steady
State Conversion Ratios

The relationship between the sum of PHBrL(BD) and
PHOBrL and the required composition of a
NaBr/trichloroisocyanuric acid (ACL90 PLUS) composition is
summarized in Figure 6. The line labeled 'CR = 1.0' gives
the relationship between PHBrL(BD) + PHOBrL and the weight
% NaBr required in the composition to produce a Conversion
Ratio of 1.0. For instance, for a tower with a bromide
ion loss rate of 3.3%/hour the NaBr/trichloroisocyanuric
acid composition should be 4.8% NaBr. The lines marked
'CR = 4.0' and 'CR = 0.5' give the relationship for the
extremes of the most preferred Conversion Ratio. The

dashed arrow at 4% NaBr shows that a composition of 4%
NaBr/96% trichloroisocyanuric acid can maintain the
Conversion Ratio in the most preferred range of 0.5 to 4.0
for towers for PHBrL(BD) + PHOBrL = 0.75%/hour to well
5   over 5%/hour. This range covers virtually all common
cooling tower systems. In contrast, a composition with
only 2% NaBr/98% trichloroisocyanuric acid will maintain
the Conversion Ratio in the most preferred range only for
PHBrL(BD) + PHOBrL between 0.38 and 2.5%/hour. Many
10   common cooling towers have larger bromide ion loss rates
than this, as was shown in Examples 3 and 4.

This example shows the importance of understanding
the relationship between the total bromide ion loss rate
15   and the sodium bromide content of ACL90 PLUS/NaBr
compositions and the capabilities of these compositons to
attain and maintain the desired Conversion Ratios,
especially those that enable these compositions to perform
as bromine biocides. These same relationships also exist
20   for other hypochlorite donor/bromide ion donor
compositions and/or combinations. These relationships can
be established with the methods described herein.

For cooling tower operations subject to EPA discharge
25   limits of 0.2 ppm (available chlorine basis), it is
preferred to maintain the Conversion Ratio at or above
one, since hypobromite species dissipate faster than
hypochlorite species.

30   For use in air washers, it is preferred that the
Conversion Ratio be maintained at or above a value of one
since it is important to eliminate all chlorine or
chloramine odors from the air passed through the air
washer. Odor is more important in air washers than in
35   cooling towers since the washed air is used inside
buildings, factories, and the like. Thus, somewhat higher

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percentages of NaBr are required for compositions of this
invention used in cooling tower operations subject to EPA
limits and in air washers. For instance, Figure 6 shows
that a 4% NaBr/96% trichloroisocyanuric acid composition
5   will maintain the Conversion Ratio in the preferred range
of 1.0 to 4.0 for PHBrL(BD) + PHOBrL = 0.75% to
2.75%/hour. If the loss rate is higher, a composition
with a higher NaBr percentage would be necessary.

10

Example 14 - Demonstration of Bromide Ion Loss From Spas

This example demonstrates the magnitude of bromide
ion loss that can occur in a commercial spa. A spa with a
15   capacity of 1000 gallons of water was chlorinated
continuously with ACL90 PLUS (trichloroisocyanuric acid)
around the clock to maintain a free chlorine concentration
of 2 ppm. The spa water was maintained at a temperature
of 40°C. The water was aerated only during the day, the
20   high bather load period, for about 12 hours. Sufficient
sodium bromide was added to the spa water to obtain a
bromide ion concentration of 3 ppm. This is the amount
required to attain a Conversion Ratio of 1.33 versus the
optimum of 1.0 and to make the chemicals perform as a
25   bromine sanitizer. Water samples were taken about every
four hours for several days. The analyses showed that the
bromide ion concentration decreased steadily from 3 to 1
ppm over a period of 6 days. The chlorine demand was
about 10 ppm per day (available chlorine basis). During
30   this period, the odor of the air above the spa changed
gradually from that of bromamines to chloramines. These
results demonstrated that bromide ion was lost from the
water and that the hypohalite species were a mixture of
hypochlorite and hypobromite species. As a consequence,
35   the biocide performed more like a chlorine sanitizer than
a bromine sanitizer.

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Example 15 - Control of Optimum Conversion Ratio in Spas
with ACL90 PLUS/NaBr Compositions

         This example further demonstrates how knowledge of
5   the bromide ion loss can be applied to the development of
     the appropriate sanitizer compositions. The results in
     Example 14 show that the bromide ion loss rate was about
     0.33 ppm/day. This means that at least 2.5 grams must be
     added daily to maintain the desired concentration. The
10   chlorine demand during this period was about 10 ppm/day,
     which corresponds to a ACL90 PLUS consumption rate of 41.3
     grams/day. These results indicate that to satisfy the
     chlorine demand and bromide ion loss requirements with a
     product made of the two materials, the product must
15   contain ACL90 PLUS and sodium bromide in the weight
     proportions of 41.3 to 2.5. Thus, the tablet for this
     application must contain at least 94.3 wt % ACL90 PLUS and
     5.7 wt % sodium bromide.

20   To demonstrate the utility of this concept, an ACL90
     PLUS/sodium bromide mixture with 6% NaBr was compacted
     into one-inch tablets weighing 15 grams each. The tablets
     were placed in a standard erosion feeder where the water
     flow was adjusted to maintain the desired free halogen
25   concentration of 2 ppm (available chlorine basis). Water
     samples were then taken periodically for six days. The
     bromide analyses showed that the bromide ion concentration
     built up steadily to the desired concentration and
     remained constant for the remainder of the test, thereby
30   insuring that this product was performing as a bromine
     sanitizer.

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Bromine Volatilization Suppressant

It has also been discovered that, in addition to
simply adding enough bromide ion donor to compensate for
5   all bromide ion losses, it is possible to approach the
problem in a second way, that is, by reducing or
suppressing the amount of volatilization of HOBr and
bromamines. This can be accomplished by addition of a
hypobromous acid volatilization suppressant compound. The
10   volatilization suppressant must bind free bromine species
(HOBr) strongly enough to reduce the concentrations of
hypobromous acid and bromamine significantly, but not so
strongly that the disinfecting properties of the bromine-
based biocide will be reduced. In addition, the
15   volatilization suppressant must be chemically compatible
with the hypochlorite donor compounds in the single
product compositions to be fed to the tower.

Cyanuric acid has been used in swimming pools to
20   reduce the decomposition of hypochlorous acid by the UV
rays of sunlight and in cooling towers to reduce the loss
of free chlorine. However, cyanuric acid will not
suppress the loss of free bromine by volatilization and
degradation in sunlight because cyanuric acid does not
25   bind free bromine as strongly as it does free chlorine.

It has been found that hydantoin derivatives (such as
DMH); sulfonamide derivatives; sulfamic acid derivatives;
glycoluril derivatives; oxazolidinone derivatives;
30   imidazolidinone derivatives; and succinimide derivatives
are capable of acting as volatilization suppressants for
free bromine. However, it was discovered that when
hydantoin derivatives are used, the concentration of the
volatilization suppressant relative to the concentration
35   of the free bromine must be controlled in order to avoid

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significant reduction in the biocidal activity of the
biocides of the present invention.

DMH can be used to reduce bromide ion losses by
5 reducing volatilization loss by as much as 85% before it
begins to have a deleterious effect on the disinfection
properties of the bromine-based biocide according to the
present invention. However, DMH concentrations more than
ten times the hypobromous acid concentration (expressed in
10 terms of free available chlorine) can significantly
decrease the biocidal effectiveness of the hypobromous
acid. For example, if the free halogen level in the
recirculating water is controlled at 0.5 mg/L (free
available chlorine basis), DMH concentrations greater than
15 5.0 mg/L must be avoided. DMH concentrations of over 50
mg/L can easily be reached if BCDMH is used as the
biocide. Because of the potential for reducing the
effectiveness of bromine-based biocides, the concentration
of DMH or other stabilizer compounds should be maintained
20 at an appropriately low level, preferably less than 10 ppm
in the case of DMH.

Example 16 - Demonstration of the Effect of
25   Dimethylhydantoin on Bromide Ion Losses

This example demonstrates how bromide ion losses can
be significantly reduced with bromine volatilization
suppressants.
30
In this particular experiment, the cooling water of
Example 4 was dosed with enough sodium bromide to obtain a
Conversion Ratio of about one. DMH was then added to the
water in an amount sufficient to attain a concentration of
35 20 ppm. Again, lithium chloride was used as a tracer.
The water was recirculated for about one hour to obtain a

uniform distribution of chemicals. Water samples were
then taken periodically for the next 24 hours and analyzed
for bromide, lithium and DMH. The results are tabulated
in Table 5.

5

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TABLE 5

Effect of DMH on Bromide Ion Losses

Water Sample	Time Hr.	Bromide Ion Concentration ppm	DMH Concentration ppm	Lithium Concentration ppm	Bromide Ion Losses (%)
1	1	0.5	21	0.45	0
2	2	0.5	20	0.44	0
3	3	0.5	19	0.42	0
4	4	0.48	20	0.42	4
5	8	0.46	20	0.42	8
6	16	0.42	19	0.41	18
7	24	0.38	18	0.42	24

These data demonstrate that bromide ion losses were reduced dramatically with the addition of DMH, thus establishing another way to compensate for bromide ion losses via the volatilization pathway.

Example 17 - Effect of DMH on Henry's Law Constants for Hypobromous Acid

The previous example demonstrated that DMH could be used to obtain significant reductions in bromide ion losses from cooling water systems containing the hypochlorite donor/bromide ion donor compositions described in this invention. This example shows the effect of the DMH concentration on the tendency of the bromide ion to be lost from cooling waters by volatilization. Just as important, it provides data critical to controlling the DMH concentration so that the excellent biocidal properties of these bromine biocide compositions are not compromised by high DMH residuals.

The effect of DMH concentration was demonstrated by determining the Henry's Law constants for a series of

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solutions in which the available halogen, bromide, pH and temperature were held constant but the DMH concentration was varied.

5   The results of these experiments are tabulated in Table 6 and shown graphically in Figure 7.

Table 6

10

Effect of DMH on Henry's Law Constants For
Solutions Containing Hypohalite Species and
Bromide Ion

15   Experimental Conditions

pH = 8.5

Temperature = 22.5°C

20

Free halogen (as Cl_2) = 2 mg/L

Bromide ion = 2.25 mg/L

25 DMH/Free Bromine Mole Ratio	Henry's Law Constant H_k
0.0	0.220
2.0	0.037
30 5.0	0.028
10.0	0.024
30.0	0.019

Depicting these results graphically, Figure 7 shows
35 that the Henry's Law constant decreased significantly as the DMH/free bromine mole ratio increased from 0 to 10, but decreased very little above 10. These results indicate that there is no need to use DMH/free bromine ratios of greater than 10. More importantly, killing
40 efficiency data show that the biocidal properties begin to decrease significantly above this ratio.

The foregoing description has been directed to particular embodiments of the invention for the purposes

of illustration and explanation. It will be apparent,
however, to those skilled in this art that many
modifications and changes in the compositions and methods
set forth will be possible without departing from the
5 scope and spirit of the invention. It is intended that
the following claims be interpreted to embrace all such
modifications and changes.

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WHAT IS CLAIMED IS:

1.   A biocidal composition for use in recirculating water systems comprising a hypochlorite donor and a bromide ion
5   donor, wherein the composition contains an amount of the bromide ion donor effective to maintain a mole ratio of the sum of all bromine containing species to the sum of all hypohalite species in the recirculating water of about 0.2 to about 20.
10

2.   The composition of claim 1 wherein

         the hypochlorite donor is an alkali metal
15   hypochlorite, an alkaline earth metal
                 hypochlorite, a chlorinated hydantoin, a
                 chlorinated oxazolidinone, a chlorinated
                 imidazolidinone, or a chlorinated isocyanuric
                 acid derivative; and
20
         the bromide ion donor is an alkali metal bromide, an
                 alkaline earth metal bromide, R_4-ammonium
                 bromide where R is any alkyl or aryl group, a
                 bromamine, a N-brominated hydantoin, a N-
25   brominated sulfonamide, a N-brominated
                 succinimide, a N-brominated oxazolidinone, a N-
                 brominated imidazolidinone, a N-brominated
                 isocyanurate, or a salt of a trihalide or mixed
                 trihalide ion containing bromine.
30

3.   The composition of claim 2 wherein the hypochlorite donor is a chlorinated isocyanuric acid derivative.

35

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4.   The composition of claim 3 wherein the chlorinated
isocyanuric acid derivative is sodium dichloro-s-
triazinetrione, potassium dichloro-s-triazinetrione, a
hydrate of sodium or potassium dichloro-s-triazinetrione,
5   dichloroisocyanuric acid, trichloroisocyanuric acid,
[mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-
triazinetrione, [mono(trichloro)-mono (monopotassium
dichloro)]-di-s-triazinetrione, or mixtures thereof.

10

5.   The composition of claim 4 wherein the hypochlorite
donor is trichloroisocyanuric acid and the bromide ion
donor is sodium bromide or potassium bromide.

15

6.   The composition of claim 4 wherein the hypochlorite
donor is an alkali metal dichloroisocyanurate and the
bromide ion donor is sodium bromide or potassium bromide.

20

7.   The composition of claim 1, 2, 3, 4, 5 or 6
comprising:

from about 85 parts by weight to about 99 parts by
25   weight of the hypochlorite donor; and

from about 1 part by weight to about 15 parts by
          weight of the bromide ion donor.

30

8.   The composition of claim 4 wherein the hypochlorite
donor is trichloroisocyanuric acid and the bromide ion
donor is a brominated hydantoin.

35

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9.   The composition of claim 8 wherein the brominated
hydantoin is a bromochlorohydantoin.

5 10.   The composition of claim 2 wherein the hypochlorite
donor is a dichlorohydantoin and the bromide ion donor is
a bromochlorohydantoin.

10 11.   The composition of claim 1, 2, 3, 8, 9 or 10
comprising:

         from about 50 parts by weight to about 99 parts by
              weight hypochlorite donor;

15
         from about 1 part by weight to about 50 parts by
              weight bromide ion donor.

20 12.   A biocidal composition for use in recirculating water
systems comprising a hypochlorite donor, a bromide ion
donor, and a bromine volatilization suppressant, wherein
the composition contains an amount of the bromide ion
donor effective to maintain a mole ratio of the sum of all
25 bromine containing species to the sum of all hypohalite
species in the recirculating water of about 0.2 to about
20.

30 13.   The composition of claim 12 wherein:

         the hypochlorite donor is an alkali metal
              hypochlorite, an alkaline earth metal
              hypochlorite, a chlorinated oxazolidinone, a
35   chlorinated imidazolidinone, or a chlorinated
              isocyanuric acid derivative;

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the bromide ion donor is an alkali metal bromide, an
        alkaline earth metal bromide, R_4-ammonium
        bromide where R is any alkyl or aryl group, a
        bromamine, a N-brominated sulfonamide, a N-
5   brominated succinimide, a N-brominated
        oxazolidinone, a N-brominated imidazolidinone, a
        N-brominated isocyanurate, or a salt of a
        trihalide or mixed trihalide ion containing
        bromine; and

10

the bromine volatilization suppressant is a hydantoin
        derivative, a sulfonamide derivative, a sulfamic
        acid derivative, a glycoluril derivative, a
        succinimide derivative, an oxazolidinone
15   derivative, or an imidazolidinone derivative.

14. The composition of claim 13 wherein the hypochlorite
donor is trichloroisocyanuric acid, the bromide ion donor
20 is sodium bromide or potassium bromide, and the bromine
volatilization suppressant is dimethylhydantoin.

15. The composition of claim 13 wherein the hypochlorite
25 donor is a alkali metal dichloroisocyanurate, the bromide
ion donor is sodium bromide or potassium bromide, and the
bromine volatilization suppressant compound is
dimethylhydantoin.

30
16. The composition of claim 12, 13, 14 or 15 comprising:

        from about 85 parts by weight to about 98 parts by
                weight hypochlorite donor;

35

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from about 1 part by weight to about 15 parts by
weight bromide ion donor; and

from about 1 part to about 10 parts by weight bromine
5   volatilization suppressant.

17.   The composition of claim 12 wherein the hypochlorite
donor, the bromide ion donor, and the bromine
10   volatilization suppressant are dry, water-soluble solids.

18.   The composition of claim 17 wherein the solids are
compacted in the form of tablets, sticks or pucks.
15

19.   The composition of claim 18 further comprising a
compacting aid.

20

20.   The composition of claim 19, wherein the compacting
aid is one or more of boric acid, sodium stearate,
potassium stearate, aluminum hydroxide, or monoglycerol
stearate.
25

21.   A method of controlling biofouling and microorganism
population levels in recirculating water systems which
comprises adding to the system either separately or
30   together in a combination or mixture, an amount of a
hypochlorite donor and a bromide ion donor which is
effective to maintain a mole ratio of the sum of all
bromine containing species to the sum of all hypohalite
species dissolved in the recirculating water of about 0.2
35   to about 20.

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22.   The method of claim 21 wherein the hypochlorite donor
is:

gaseous chlorine, an alkali metal hypochlorite, an
5   alkaline earth metal hypochlorite, a chlorinated
           hydantoin, a chlorinated oxazolidinone, a
           chlorinated imidazolidinone, or a chlorinated
           isocyanuric acid derivative; and

10   said bromide ion donor is liquid bromine, bromine
           chloride, an alkali metal bromide, an alkaline
           earth metal bromide, R_4-ammonium bromide where R
           is any alkyl or aryl group, a bromamine, a N-
           brominated hydantoin, a N-brominated
15   sulfonamide, a N-brominated succinimide, a N-
           brominated oxazolidinone, a N-brominated
           imidazolidinone, a N-brominated isocyanurate, or
           a salt of a trihalide or mixed trihalide ion
           containing bromine.

20

23.   The method of claim 22 wherein the hypochlorite donor
is a chlorinated isocyanuric acid derivative.

25

24.   The method of claim 23 wherein the chlorinated
isocyanuric acid derivative is sodium dichloro-s-
triazinetrione, potassium dichloro-s-triazinetrione, a
hydrate of sodium or potassium dichloro-s-triazinetrione,
30   dichloroisocyanuric acid, trichloroisocyanuric acid,
[mono(trichloro)-tetra(monopotassium dichloro)]-penta-s-
triazinetrione, [mono(trichloro)-mono (monopotassium
dichloro)]-di-s-triazinetrione, or mixtures thereof.

35

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25.   The method of claim 24 wherein the hypochlorite donor
is trichloroisocyanuric acid and the bromide ion donor is
sodium bromide or potassium bromide.

5

26.   The method of claim 24 wherein the hypochlorite donor
is an alkali metal dichloroisocyanurate and the bromide
ion donor is sodium or potassium bromide.

10

27.   The method of claim 21, 22, 23, 24, 25 or 26 wherein
said mixture comprises;

        from about 85 parts by weight to about 99 parts by
15   weight of a hypochlorite donor; and

        from about 1 part by weight to about 15 parts by
                weight of a bromide ion donor.

20

28.   The method of claim 24 wherein the hypochlorite donor
is trichloroisocyanuric acid and the bromide ion donor is
a brominated hydantoin.

25

29.   The method of claim 28 wherein the brominated
hydantoin is bromochlorohydantoin.

30   30.   The method of claim 22 wherein the hypochlorite donor
is a dichlorohydantoin and the bromide ion donor is a
bromochlorohydantoin.

35   31.   The method of claim 21, 22, 23, 28, 29 or 30 wherein
said mixture or combination comprises:

from about 50 parts by weight to about 99 parts by
    weight hypochlorite donor; and

from about 1 part by weight to about 50 parts by
5   weight bromide ion donor.

32. A method of controlling biofouling and microorganism
population levels in recirculating water systems which
10 comprises adding to the system, separately or together in
a combination or mixture, an amount of a hypochlorite
donor, a bromide ion donor, and a bromine volatilization
suppressant which is effective to maintain a mole ratio of
the sum of all bromine containing species to the sum of
15 all hypohalite species dissolved in the recirculating
water of about 0.2 to about 20.

33.   The method of claim 32 wherein:
20

the hypochlorite donor is gaseous chlorine, an alkali
        metal hypochlorite, an alkaline earth metal
        hypochlorite, a chlorinated oxazolidinone, a
        chlorinated imidazolidinone, or a chlorinated
25   isocyanuric acid derivative;

the bromide ion donor is liquid bromine, bromine
        chloride, an alkali metal bromide, an alkaline
        earth metal bromide, R_4-ammonium bromide where R
30   is any alkyl or aryl group, a bromamine, a N-
        brominated sulfonamide, a N-brominated
        succinimide, a N-brominated oxazolidinone, a N-
        brominated imidazolidinone, a N-brominated
        isocyanurate, or a salt of a trihalide or mixed
35   trihalide ion containing bromine; and

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the bromine volatilization suppressant is a hydantoin
derivative, a sulfonamide derivative, a sulfamic
acid derivative, a glycoluril derivative, a
succinimide derivative, an oxazolidinone
5   derivative, or an imidazolidinone derivative.

34. The method of claim 33 wherein the hypochlorite donor
is trichloroisocyanuric acid, the bromide ion donor is
10 sodium bromide or potassium bromide, and the bromine
volatilization suppressant is dimethylhydantoin.

35. The method of claim 33 wherein the hypochlorite donor
15 is an alkali metal dichloroisocyanurate, the bromide ion
donor is sodium bromide or potassium bromide and the
bromine volatilization suppressant is dimethylhydantoin.

20 36. The method of claim 32, 33, 34 or 35 wherein said
mixture or combination comprises:

from about 85 parts by weight to about 99 parts by
weight hypochlorite donor;
25

from about 1 part by weight to about 15 parts by
weight bromide ion donor; and

from about 1 part to about 15 parts bromine
30   volatilization suppressant.

37. The method of claim 32 wherein the hypochlorite
donor, the bromide ion donor and the bromine
35 volatilization suppressant are dry, water-soluble solids.

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38. The method of claim 37 wherein the solids are compacted in the form of tablets, sticks or pucks.

5 39. The method of claim 38 wherein the mixture or combination further comprises a compacting aid.

40. The method of claim 39 wherein the compacting aid is 10 one or more of boric acid, sodium stearate, potassium stearate, aluminum hydroxide, or monoglycerol stearate.

41. The method of claim 21 wherein the mixture or 15 combination is introduced into the recirculating water system by any of the following means: an erosion feeder, a floater, porous bags, perforated buckets or hand dosing.

20 42. The method of claim 21 further comprising the step of introducing an effective amount of one or more scale inhibitors into the recirculating water.

25 43. The method of claim 42 wherein the scale inhibitor is included in the mixture of hypochlorite donor and bromide ion donor.

30 44. The method of claim 43 wherein the scale inhibitor is one or more of polymaleic acid, polyacrylic acid, a phosphonate, or a polyphosphate.

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45. The method of claim 21 wherein the recirculating
water system is an air washer, swimming pool or spa and
said ratio is at least 1.

5

46. A method of controlling biofouling and microorganism
population levels in a recirculating water system which
comprises adding a hypochlorite donor and a bromide ion
donor to the system in quantities sufficient to form and
10 maintain hypobromous acid in the system, the quantity of
bromide ion donor being sufficient to compensate for
losses of bromide ion from the system due to blowdown,
volatilization of bromine compounds from the system, and
formation of stable organobromine compounds.
15

47. A method of maintaining a concentration hypobromous
acid in a recirculating water system sufficient to reduce
the microorganism population in the system to a desired
20 level which comprises:

        ascertaining the chlorine demand of the system and
            the rate of bromide ion loss from the system due
            to blowdown, volatilization, and formation of
25   stable organobromine compounds; and

        adding a hypochlorite donor and a bromide ion donor
            to the system in quantities sufficient to
            provide said concentration of hypobromous acid
30   in the system and maintain a mole ratio of the
            sum of all bromine containing species to the sum
            of all hypohalite species of about 0.2 to about
            20.
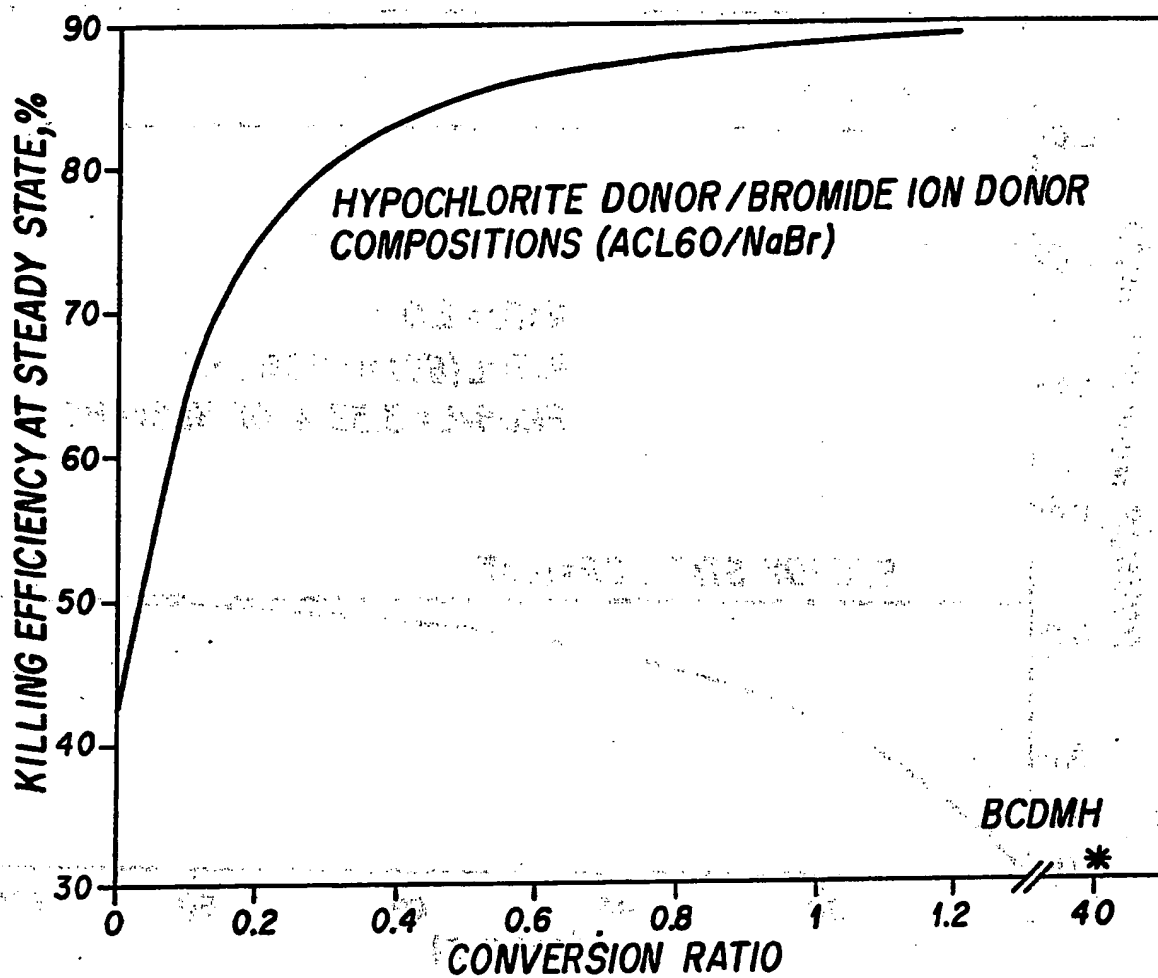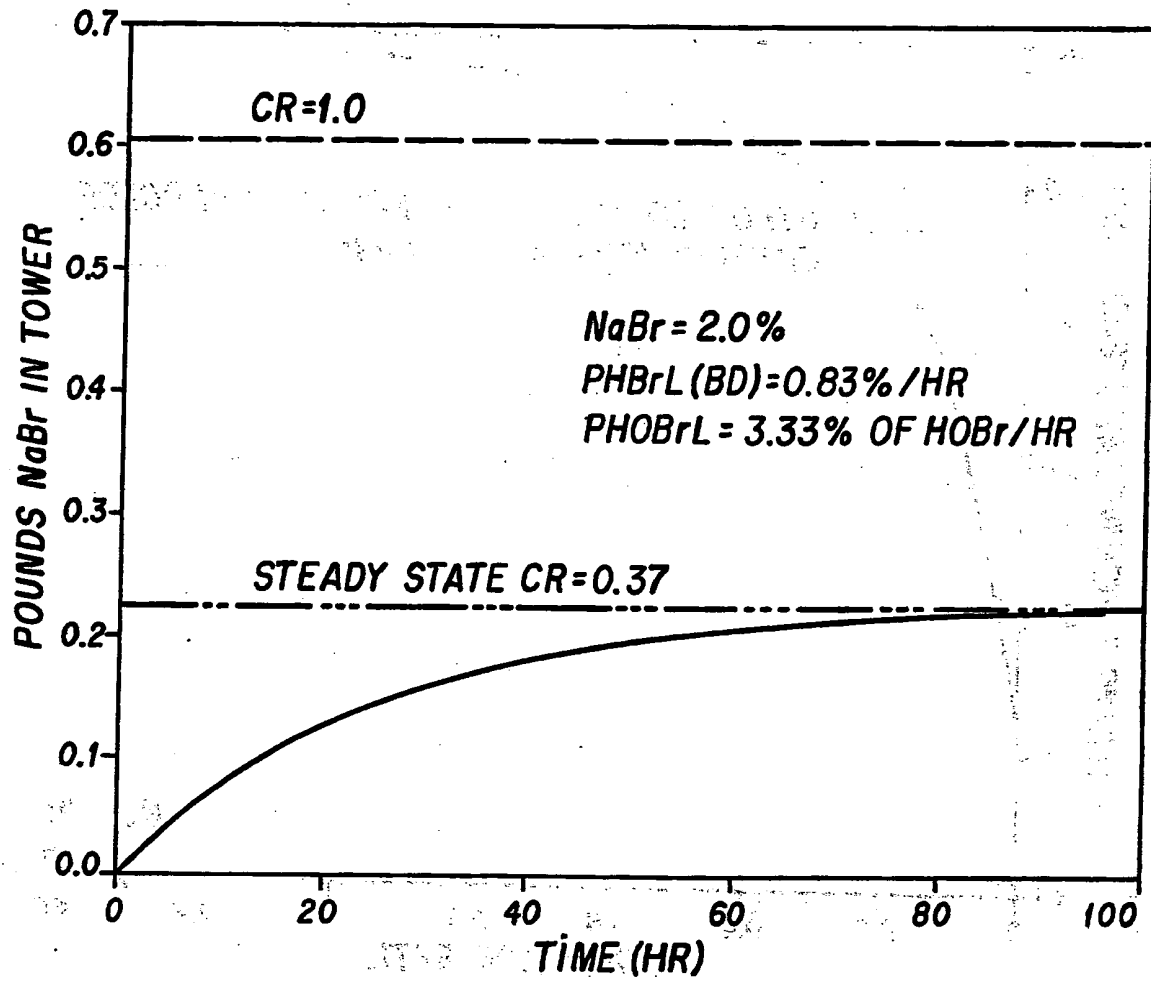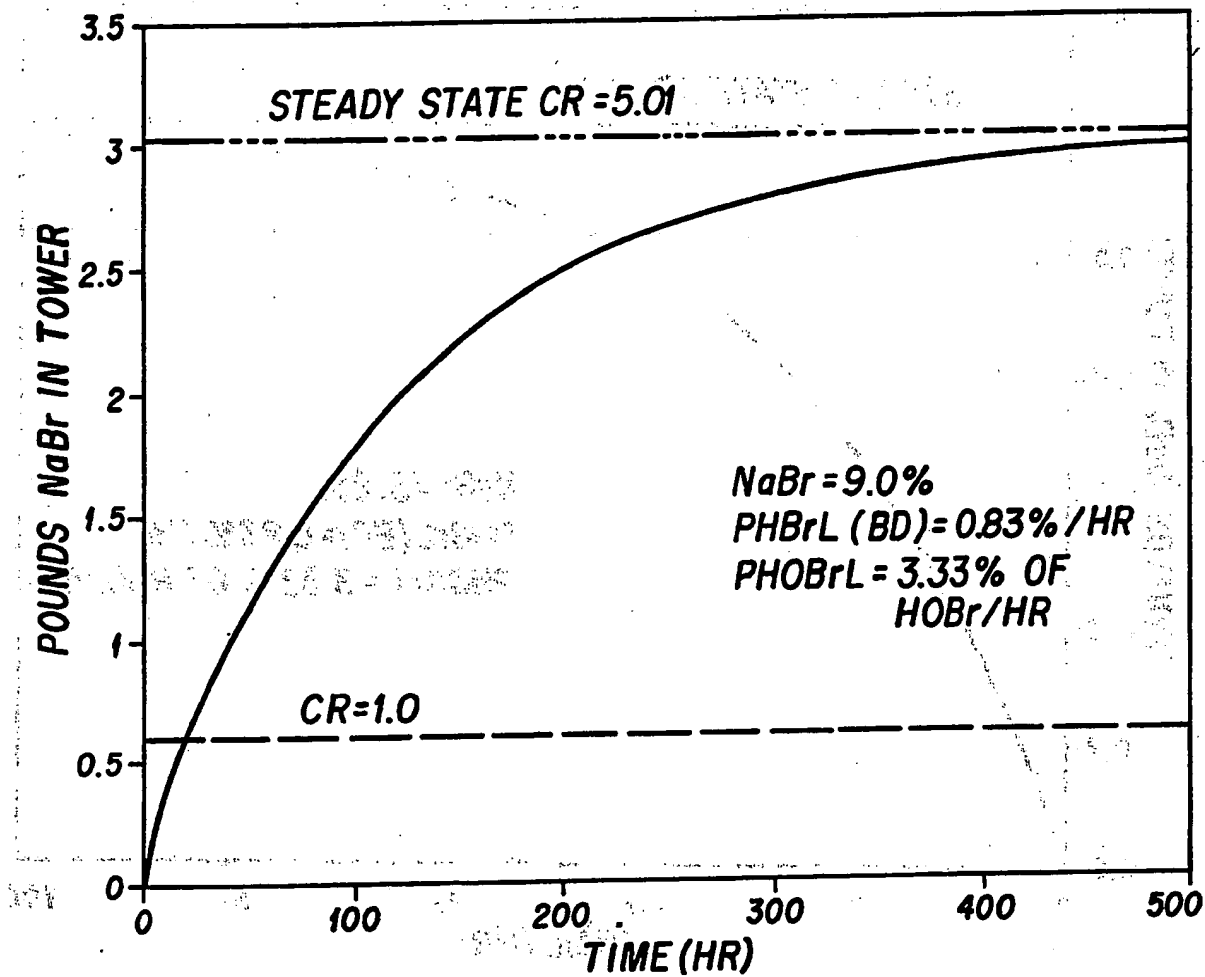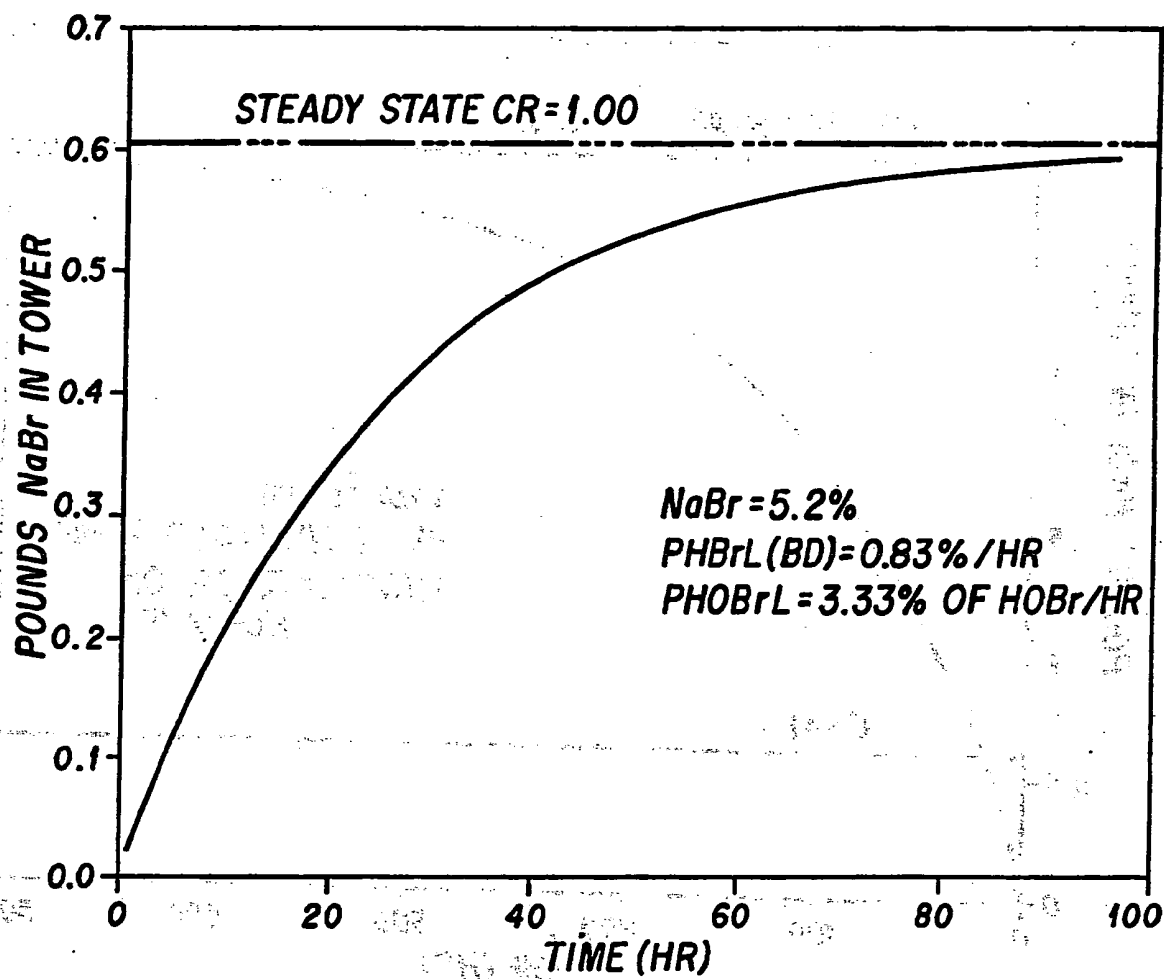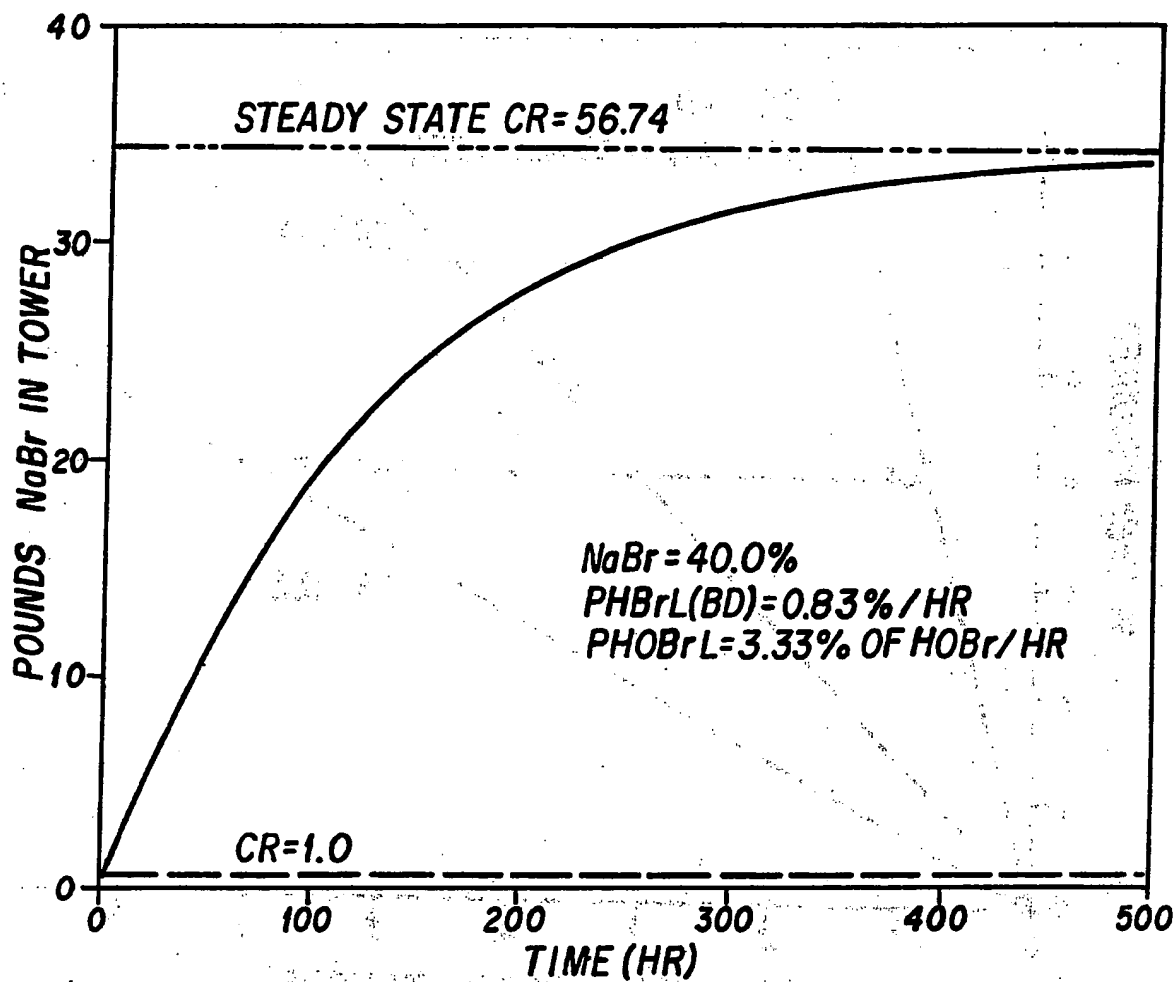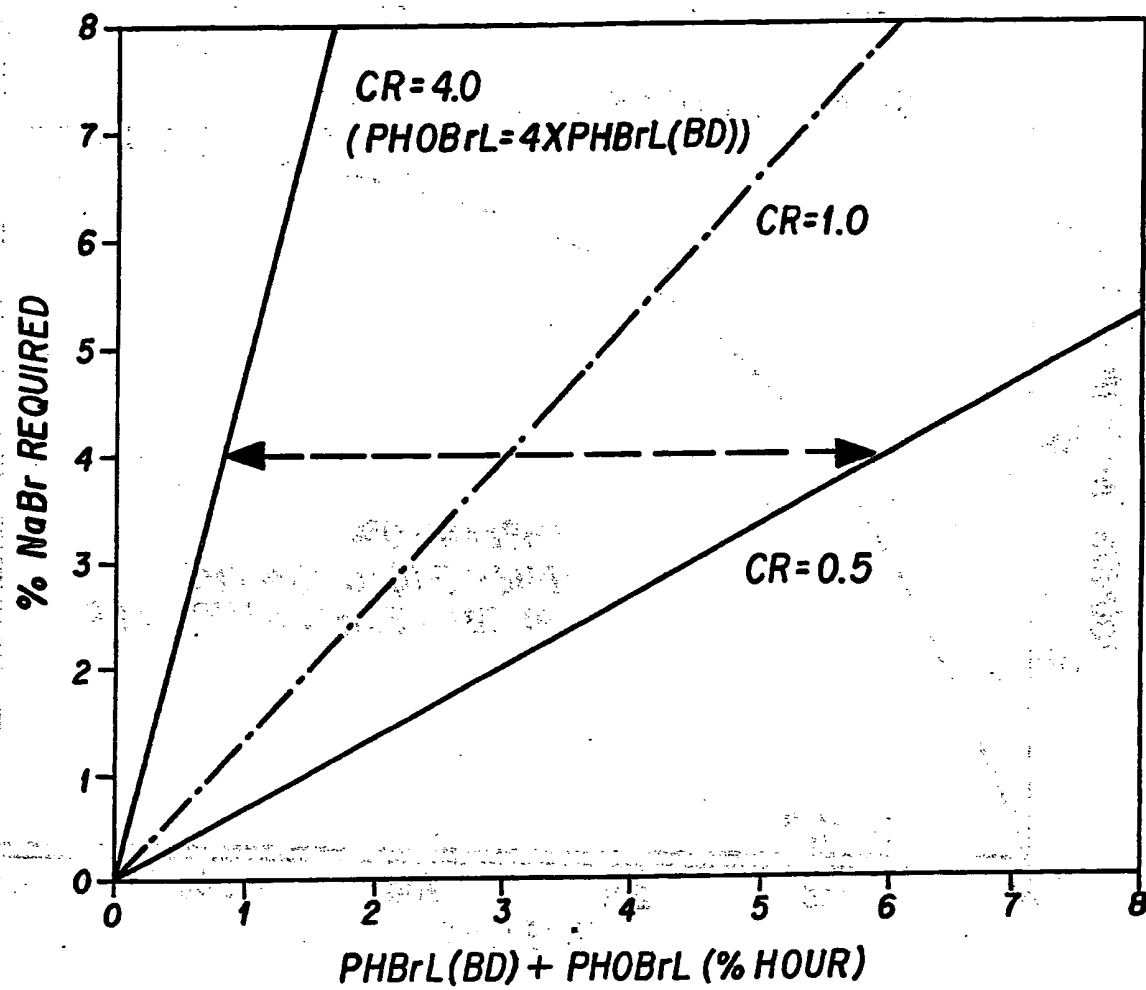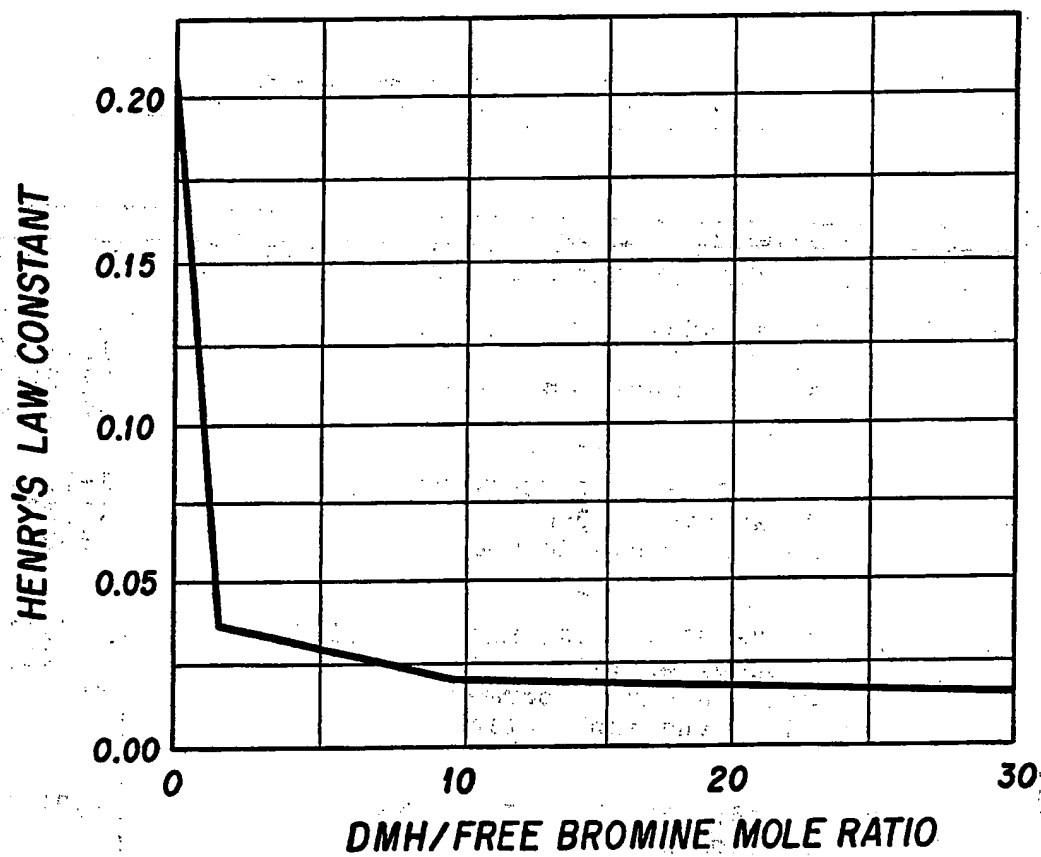
FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 02 F 1/76, 1/50, 5/08

II. FIELDS SEARCHED

Minimum Documentation Searched [7]	
Classification System	Classification Symbols
IPC[5]	C 02 F, A 01 N

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 4759852 (M.G. TRULEAR) 26 July 1988 see the whole document	1-2,5-7,11- 13,16,21-22, 27,32-33,36, 42-44,46-47
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X	US, A, 2815311 (J.G. ELLIS et al.) 3 December 1957 see the whole document (cited in the application)	1-7,11,17- 18,21,42- 44
X	US, A, 4698165 (T.W. THEYSON) 6 October 1987 see the whole document	1,21-22
	./.	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
27th September 1990	19. 10. 90
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	Mme N. KUIPER

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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P,X	US, A, 4846979 (J. HAMILTON) 11 July 1989 see the whole document	1-2,42-47
X	DE, A, 2042254 (FISONS) 4 March 1971 see pages 1,6-7,10,15-16	1,21,31,37-42
X	US, A, 4451376 (J.D. SHARP) 29 May 1984 see the whole document (cited in the application)	1-2,44
P,X	US, A, 3412021 (L.O. PATERSON) 19 November 1968 see the whole document	1-11
A	(cited in the application)	12-20
X	GB, A, 1327531 (MINES DE POTASSE etc.) 22 August 1973 see claims (cited in the application)	47

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9003139
SA 37891

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 15/10/90
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